Pollutant Emissions from Biodiesels in Diesel Engine Tests

and On-road Tests

By

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Submitted to the graduate degree program in Civil, Environmental, and Architectural Engineering and the Graduate Faculty of the University of Kansas in partial fulfillment of the requirements for the degree of Master of Science.

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Abstract

Interest in biodiesel use is increasing due to concerns over the availability and environmental impact of petroleum fuels. In this study, we analyzed biodiesels prepared from seven different feedstocks: waste cooking oil, rapeseed oil, olive oil, palm oil, coconut oil, canola oil, and soybean oil. Exhaust emissions of gas-phase compounds (CO_2, CO, NO_2, NO, THC) and particulate matter were measured for each biodiesel and Ultra Low Sulfur Diesel (ULSD) during combustion in a diesel generator operating under different engine loads (0, 25, 50, 75, 100%). The composition of each biodiesel was also analyzed using a variety of chemical and physical tests to investigate the relationship between fuel properties and pollutant emissions.

The results showed that both engine performance and biodiesel composition affected emissions levels. All brake-specific emissions decreased with increased of engine load because of high fuel efficiency at high loads. All of the biodiesels except coconut oil produced less THC emissions than ULSD, and soybean oil, palm oil, olive oil produced less CO than ULSD. Particulate matter emissions were reduced for all biodiesel fuels compared to ULSD. However, CO_2 emissions from biodiesels were higher than ULSD. NO emissions from biodiesels were higher than ULSD at low load, but some of them started (ex. Palm oil) to perform better with increased load, and finally produced less NO than ULSD. All biodiesel produced less NO_2 than ULSD. Considering NOx emissions in unit of g/kg fuel, NO increased and NO_2 decreased with increased engine

loads, resulting in highest total NOx emissions at 50% to 75% load, depending on the fuel. NO was the majority of total NOx emission. Biodiesel oxygen content was strongly correlated to PM and HC emissions. The H: C ratio, ratio of saturated fatty acids and degree of unsaturation of biodiesels all had a substantial effect on NO emissions. Density measurement was an easy way to predict total NOx from biodiesels.

Methods of running on-road biodiesel truck tests and data analysis were developed. Both road condition and engine performance affected the formation of emissions. Vehicle specific power (VSP) was calculated to present real power required in on-road tests. Tests data of highways showed that CO and HC emissions (g/kg/fuel) decreased with the increase of VSP.

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Chapter 1

Introduction and Background

1.1 Air pollution

Air pollution can be caused both by natural events (volcanic eruptions, forest fires, etc.) and by human activities. With industrialization around the world, air pollution originating from combustion, industrial processes, transport and agriculture has become one of the most serious widespread environmental and public health problems now. The World Health Organization (WHO) states that air pollution causes approximately 2 million premature deaths worldwide every year [1].

In fact, air pollution is nothing new. The City of London in England is a good example of air pollution both in history and nowadays. As early as the 13th century, black smoke became a big problem in London. In order to solve the smoke problem, King Edward I issued a proclamation to regulate the burning of coal, which was the first regulation for improving air quality in history [2]. However, many of the worst air pollution events still occurred in the last two centuries in London because of its large population and high degree of industrialization. The most serious one happened in 1952. The temperature inversion trapped fog laden with pollutants created by burning coal for five days, and more than 4000 people died because of this deadly black fog [3]. This event prompted Great Britain to pass a Clean Air Act in 1956. Today, smog caused by

traffic pollution still does occur in modern London. The City of London is still one of the most polluted places in Europe and the air pollution could be contributing to up to 50,000 deaths in UK a year [4].

As another industrial power with rapid development, the United States began to have air pollution events during the 1940s. Los Angeles, California was one of the first cities experiencing severe air pollution problems because of its location. The auto exhausts and emissions from petroleum refineries were readily accumulated in this area as the city was surrounded by mountains. In 1948, emissions from zinc smelting and blast furnaces failed to disperse under a temperature inversion, which caused 20 people to die, 600 others to become ill, and 1400 to need medical attention [3]. Although Los Angeles has been become a pioneer of stricter emission regulations and has advanced technology for air pollution control, its air pollution problems have not been totally solved. In California as a whole, more than 3,800 premature deaths and 466,800 lost days of work happen annually, which can be avoided if air quality can meet federal standards [5]. According to a report of American Lung Association in 2011, air quality in many places in the US has improved but still over half of the people are suffering pollution levels that are dangerous to breathe [6], which indicates air pollution is a national problem in the US.

In addition to developed countries, more developing countries are facing air pollution problems nowadays. Beijing in China, Cairo in Egypt, Mexico City in Mexico, New Delhi in India etc, are commonly listed as “top-polluting cities” lists [7, 8]. Air pollution is becoming a worldwide issue, rather than confined to a few countries.

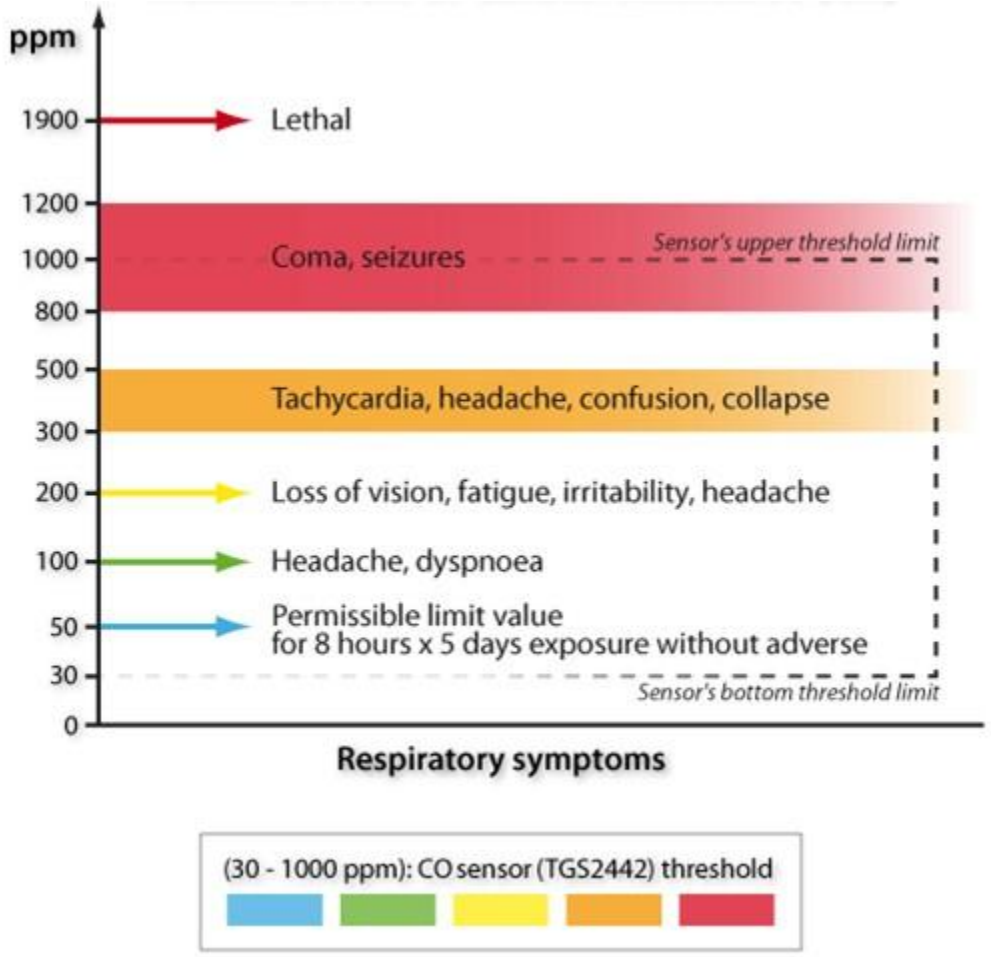
Ambient air pollutants include sulfur oxides (SOx), nitrogen oxides (NOx), carbon monoxide (CO), ozone (O_3), particulate matter (PM), lead, among others. In general, air pollutants irritate eyes, nose, and throat, and have long-term adverse health effects including chronic respiratory symptoms or illnesses, reduction of lung function, and even damage to brain, nerves, liver, or kidneys. Children, elderly people, and people with health problems such as asthma, heart and lung disease are more prone to suffer from health effects because of their poor lung function [9]. Air pollution is also a risk factor for stroke when the pollutant levels are particularly high [10].

It is important to point out that PM affects more people than any other pollutant. Because many toxins, like metals, black carbon, sulfates and nitrates, are concentrated in particulate matters, especially fine particulate matters ($PM_{2.5}$, which are less than 2.5 micrometers in diameter), and also because these fine particles can lodge deeply into the lungs due to their small size, $PM_{2.5}$ has a primary role in the adverse health effects and the long-term exposure to it increases risk of human mortality. WHO has identified particulate pollution as one of the most important contributors to health problems in Europe, and more studies show that more than 500,000 Americans die from cardiopulmonary disease every year because of breathing fine article air pollution [11]. For this reason, PM is a most important index for air quality assessment.

NOx reacts with other compounds to form small particles, which can penetrate into lungs to cause respiratory disease, and can aggravate heart disease [12]. The ground level ozone can trigger a variety of health problems like airway irritation, wheezing and breathing difficulties, inflammation, even lung damage. CO can combine with

hemoglobin to form carboxyhemoglobin (HbCO) in the blood, which prevents oxygen binding to hemoglobin, reducing the oxygen-carrying capacity of the blood. The CO effect on human health is shown in Figure 1.

Figure 1 Health Effects of Carbon Monoxide (CO) [13]



Besides doing harm to public health, pollutants have different adverse environmental effects. NOx and SOx can come back down to the earth through both dry and wet acid deposition; including acid rain. Acid rain does harm to plants by damaging their leaves, limiting the available nutrients, or increasing the toxic substances releasing from soils. Acid rain also increases the acidity of aquatic systems, such as streams and

lakes. Usually, the pH of a natural water system is between 6 and 8, and the water system has a limited ability to neutralize the acidic compounds (this ability can be called "buffer capacity"). If streams or lakes have low buffer capacities, acid rain can greatly reduce the pH of the water, which is lethal to aquatic lives. In 1985, the U.S. Environmental Protection Agency (EPA) estimated that about 50,000 streams in the U.S. and Canada are dead or dying because of acid rain. One of the most acidic lakes reported is Little Echo Pond in Franklin, New York, with the pH of 4.2 [14]. Finally, acid rain can also accelerate the decay of building materials, statues, and sculptures, damaging relics and causing economic loss. Meantime, NOx deposition may results in eutrophication in rivers and lakes, causing algae bloom, dissolved oxygen depletion, and fish death,

Greenhouse gases like carbon dioxide (CO_2), methane, nitrous oxide, and air aerosols are leading an increase of solar irradiance, therefore causing global temperature rises above the level of natural climate variability [15]. The main results of global warming are ice melting in polar areas and a sea level rise (SLR). SLR is believed related to various coastal hazards, including storm surge, inundation of low-lying areas, beach erosion, and damages to coastal infrastructures and ecosystems. So SLR can be a serious global threat, especially to low elevation countries with heavy concentration of population and economic activity in coastal regions.

Ozone depletion is another important air pollution problem. Although ground level ozone has a negative effect on human health (irritation of respiratory system, reduction of lung function etc), the ozone layer in the stratosphere is beneficial. It filters out 97%-99% of shorter wavelengths of ultraviolet light (UV rays) from the sun, which is

damaging the life forms of the earth. The most important ozone depleting substances (ODS) are human-manufactured chlorine- and bromine-containing compounds, such as chlorofluorocarbons (CFCs). Many of them are already phased out, or are controlled, and planned to be phased out in the next few decades, in order to recover the stratosphere ozone layer.

1.2 Air pollution from auto mobiles

Air pollution is particularly serious in urban areas, mainly because of heavy industry, as well as increased vehicle use. In fact, vehicle emissions have been a major cause of local pollution and even a driver of global climate change [16]. In diesel and gasoline combustion, NOx is emitted mainly as NO, with smaller amounts of NO_2, largely through the thermal NOx chemical mechanism. The emissions of NOx and volatile organic compounds (VOCs) react in the sunlight, and result in the formation of ground level ozone, a primary ingredient in photochemical smog in the atmosphere [17]. In California, 51% of NOx and 33% of reactive organic gases come from on-road mobile sources [18]. Smog reduces visibility and therefore, causes increased traffic accidents. The internal combustion engine is also a main source for CO and PM emissions in urban area, due to incomplete combustion.

Therefore, in the early 1970's, the EPA began regulating motor vehicle pollution to control and mitigate air pollution. With the use of catalytic converters and the widespread introduction of unleaded gasoline, emissions of hydrocarbon, nitrogen oxides

and lead were reduced greatly. In 2004, per-mile exhaust emissions of new cars and trucks had been reduced by 95-99% compared to 1967 model-year vehicles [19]. However, in order to further reduce air pollution problems, the enactment of tougher emissions standards can be expected, which means more technology supports and costs for new mobile design, production and distribution are needed. Table 1 shows the current federal and California standards, from which can see the pioneer role of California.

TABLE 1 Federal and California Ambient Air Quality Standards [20]

Pollutant	Averaging Time	Federal Standards		California Standards Primary
		Primary	Secondary	
Ozone	1 hr	0.12 parts per million (ppm) (235 $\mu g/m^3$)	Same as primary	0.09 ppm (180 $\mu g/m^3$)
	8hr	0.08 ppm (157 $\mu g/m^3$)	Same as primary	0.070 ppm (137 μg/m3)
PM_{10}	24 hr	150 $\mu g/m^3$	Same as primary	50 $\mu g/m^3$
	Annual arithmetic mean	50 $\mu g/m^3$	Same as primary	20 $\mu g/m^3$
$PM_{2.5}$	24 hr	65 $\mu g/m^3$	Same as primary	No separate state standard
	Annual arithmetic mean	15 $\mu g/m^3$		12 $\mu g/m^3$
CO	8 hr	9 ppm (10 mg/m^3)	None	9.0 ppm (10 mg/m^3), Lake Tahoe 6 ppm (7 mg/m^3)
	1 hr	35 ppm (40 mg/m^3)		20 ppm (23 mg/m^3)
NO_2	Annual arithmetic mean	0.053 ppm (100 $\mu g/m^3$)	Same as primary	
	1hr			0.25 ppm (470 $\mu g/m^3$)
SO_2	Annual	0.030 ppm		

	arithmetic mean	(80 μg/m^3)		
	24 hr	0.14 ppm (365 μg/m^3)		0.04 ppm (105 μg/m^3)
	3 hr		0.5 ppm (1,300 μg/m^3)	
	1 hr			0.25 ppm (655 μg/m^3)
Pb[a]	30-day average			1.5 μg/m^3
	Calendar quarter	1.5 μg/m^3	Same as primary	
Visibility	8 hr	No federal standards		Extinction coefficient of 0.23 per kilometer; visibility of 10 miles or more
Sulfates	24 hr	No federal standards		25 μg/m3
Hydrogen sulfide	1hr	No federal standards		0.03 ppm (42 μg/m3)
Vinyl chloride	24 hr	No federal standards		0.01pm (26 μg/m3)

1.3 Alternative fuels

Energy is needed in all sectors of daily life, transport, industry, services, household, etc. Therefore, it is strongly related to economic activity and is one of main motors of economic growth. With population growth and the demand for increased quality of life, energy use is expected to increase at a high rate in the future [21]. According to the statistics from U.S. Energy Information Administration, worldwide energy consumption was 449 quadrillion Btu for 2004 and 493 quadrillion Btu for 2008,

respectively, with an average increase of 2.3% per year [22]. The primary world energy source is fossil fuels, which include coal, petroleum, and natural gas (Table 2). As is well known, fossil fuels are non-renewable sources of energy because they take millions of years to form. The current rapid depletion of fossil fuels will result in their exhaustion in the near future. Also, the use of fossil fuels produces large amount of air pollutants. Due to the predicted shortage of fossil fuel and environmental concerns, research for finding a cleaner alternative fuel has become more important. The most common potential renewable energy sources are wind, solar, and hydropower. In recent years, however, the use of biomass and biogas has also increased.

TABLE 2 Worldwide fossil fuels consumption (Quadrillion Btu)

	2006	**2007**	**2008**	**2009**
Petroleum	171.5	172.8	172.2	173.1
Natural Gas	107.38	111.065	114.436	110.045
Coal	127.06	133.473	139.195	142.947

* The data above are from U.S. Energy Information Administration [23].

Almost 20% of the world's total energy is used by transportation, in which liquid fuels are the dominant source. Transportation accounts for more than 50% of world consumption of liquid fuel, and the share is estimated to rise up to 61 percent in 2035 [22]. In order to relieve the demand for petroleum-based fuel (gasoline and diesel), a renewable source of liquid fuel is needed, and biodiesel is one possibility. In the last ten years, research on biodiesel has become increasingly popular and numbers of scientific articles and patents about biodiesel have been increasing. The introduction and commercialization of biodiesel in many countries around the world is currently underway. Biodiesel provided 1.8% of the total transport fuels in 2007, and by 2008 global biodiesel

production reached 78 billion liters [24]. The use of biodiesel in transportation is promoted as a national policy in the United States and Europe, both regions have developed standards, like ASTM D6751 (ASTM = American Society for Testing and Materials) and the European standard EN 14214, to ensure the high product quality and customer confidence [25].

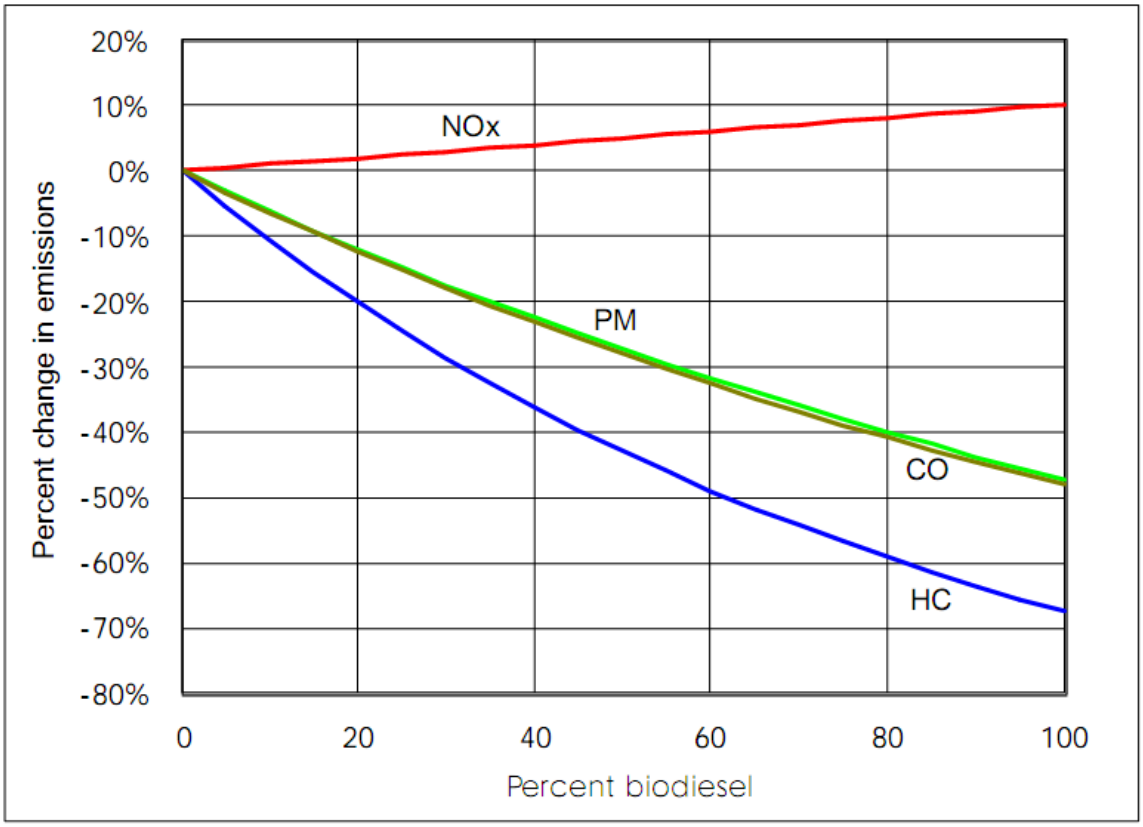
Biodiesel is a renewable fuel made from plant oil or animal fat through a trans-esterification process. The sources of biodiesel (soybean, canola, palm etc.) can be reproduced in a relatively short period of time, unlike the sources of fossil fuel (coal and oil). The constituents in biodiesel are usually short-chain esters. Biodiesel can be blended with diesel fuel at any ratio and it can be operated satisfactorily in existing diesel engines. Biodiesel's chemical constituents and properties vary greatly depending on the source of oils and fats, and this variance will affect biodiesel's engine performance and emissions.

Various oils can be used as raw materials for biodiesel production. Soybean oil is commonly used in United States and rapeseed oil is used in many European countries. Coconut oil, palm oil, canola oil, sunflower oil etc. are also been used in other areas. Waste cooking oil has also been frequently used by researchers due to its low cost [26]. The biggest advantages of esters from vegetable oils are that they do not demand any modification in diesel engine and have a high energetic yield [27].

Many studies have documented that the use of biodiesel in diesel engines can effectively reduce the CO, SOx, total hydrocarbon (THC), and PM emissions [28-30]. Figure 2 from 2002 EPA report [31] shows the emission impacts of biodiesel compared with conventional diesel, based on available data on heavy-duty highway engines. With

the use of 100% biodiesel, the average reductions of PM and CO are almost 50%, and the reduction of HC is close to 70%. In addition, net CO_2 from biodiesel is lower than it from common diesel when considering biodiesel's production cycle. However, the emissions of NOx slightly increase with the use of biodiesel. As previously stated, NOx is a precursor for ground-level ozone, and itself is harmful to human health, which has resulted in strict regulatory limits. Therefore it is important to investigate methods for reducing NOx production when biodiesel is used.

Figure 2 Average emission impacts of biodiesel for heavy-duty highway engines [31]



1.4 NOx formation in combustion

Biodiesel fuels typically produce larger amounts of NOx than diesel. Because NOx is a regulated pollutant, it is essential to find out ways to solve this problem, making sure that the use of biodiesel can still meet EPA regulations. For this reason, we need to know how NOx forms in combustion chambers.

Nitrogen gas (N_2) constitutes approximately 78.08 % by volume, 75.3 by weight of the earth atmosphere. In general, it is very stable and unreactive under standard temperature and pressure, because of the strong triple bond between N-N atoms. When air mixes with fuel in combustion process, however, the triple bond is broken due to the high temperature, allowing N to react with oxygen in the air. NOx is generally formed through the following reaction:

$N_2 + O_2 \leftrightarrow 2NO \quad \Delta G^\circ = 86.596$ KJ/mol

Generally, NOx formation is described by three methods: thermal NOx, fuel NOx, and prompt NOx. All three pathways contribute to overall NOx emissions from a fuel.

1. Thermal NOx formation

   When nitrogen and oxygen combines in the combustion chamber under relatively high temperature (>1500K), nitrogen collides with oxygen ions in the flame, and therefore thermal NO is formed. The formation of thermal NO is determined by a set of highly temperature-dependent chemical reactions known as the extended Zeldovich mechanism. The reaction equations are shown below. After the formation of thermal NO, NO reacts with additional oxygen containing

species to form NO_2. Usually, thermal NOx is the biggest contributor to NOx formation from fuel combustion [32]

$O\cdot + N_2 \leftrightarrow N\cdot + NO$ (1)

$N\cdot + O_2 \leftrightarrow O\cdot + NO$ (2)

$N\cdot + OH \leftrightarrow H\cdot + NO$ (3)

The third reaction happens particularly at near-stoichiometric conditions and in fuel-rich mixtures.

The rate constants for these equations have been determined in many experimental studies. The values below are from Hanson and Salimian [33].

$$k_{f,1} = 1.8\times10^{8} e^{-38370/T} \qquad k_{r,1} = 3.8\times10^{7} e^{-425/T}$$

$$k_{f,2} = 1.8\times10^{4} Te^{-4680/T} \qquad k_{r,2} = 3.81\times10^{3} Te^{-20820/T}$$

$$k_{f,3} = 7.1\times10^{7} e^{-450/T} \qquad k_{r,3} = 1.7\times10^{8} e^{-24560/T}$$

Note: in the equations above, $k_{f,1}, k_{f,2}$ and $k_{f,3}$ are the rates for forward reactions, respectively, and $k_{r,1}, k_{r,2}$ and $k_{r,3}$ are the rates for reverse reactions. All of the values are in the unit of m^3/gmol-s.

From the reaction equation, we see that the rate of NO formation will increase with the increased oxygen concentration, and that is also highly dependent on the temperature. Based on the rate limit of $k_{f,1}$, thermal NOx

formation doubles for every 90K temperature increase beyond 2200K. So, reducing the temperature in the combustion chamber is of primary importance in controlling NOx emissions.

2. Prompt NOx formation

Prompt NOx, which was identified by Fenimore, is a second mechanism of NOx formation. It is only generated in hydrocarbon fuel flames. It is known that a significant quantity of prompt NOx can be formed in low-temperature, fuel-rich conditions and when residence times are short [34] (Thermal NOx formation is not dominant under these conditions and hydrocarbon fragments are abundant to react with N_2). The formation of prompt NOx is complex, and many intermediate species are involved. The route can be presented as below:

$$CH\cdot + N_2 \leftrightarrow HCN + N\cdot$$

$$N\cdot + O_2 \leftrightarrow NO + O\cdot$$

$$HCN + OH \leftrightarrow CN + H_2O$$

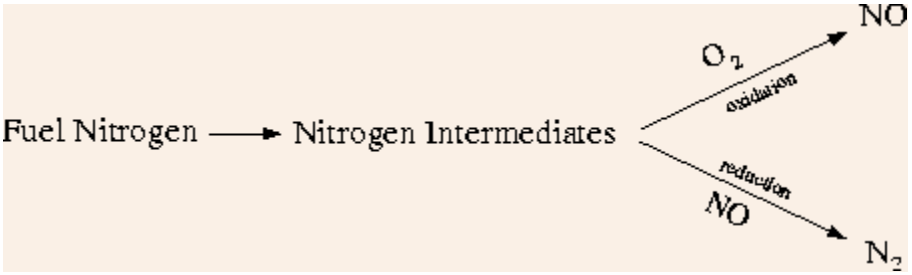
$$CN + O_2 \leftrightarrow NO + CO$$

The first reaction is of primary importance. When the fuel starts to burn, bonds in the fuel molecule break and reactive fragments are released. Some of these fragments (such as CH·) have enough energy to break the N-N bonds and form HCN molecules. The amount of HCN formed is closely related to the

concentration of CH radicals (the first step of transforming N_2 to NOx). As increased CH concentration, prompt NOx production first increases, then passes a peak, and finally decreases due to a deficiency of oxygen. Therefore, the control of fuel to air ratio is important to reduce the prompt NOx formation.

3. Fuel NOx formation

Fuel NOx is produced from nitrogen-bond compounds in fuel. Fuel-bound nitrogen-containing compounds are released into the gas phase when the fuel is heated, and radicals of HCN, NH_3, N, CN, and NH can be formed and converted to NOx. The free radicals are involved in both oxidation and reduction. The simplified model is [35]:



The energy required to break nitrate molecules down from the fuel molecule is much less than the energy to break N-N bonds, so any nitrate in fuels is a significant cause for NOx formation. However, biodiesel compounds usually do not have significant levels of nitrogen, which means fuel NOx is not a major pathway for biodiesel NOx emissions.

1.5 Literature review

The wide use of biodiesel has two requirements: biodiesel must perform well in modern diesel engines without modifications and the use of biodiesel must not increase tailpipe emissions. Numerous studies have investigated physical and chemical properties of different biodiesels, which are critical to the engine performance and emissions. Table 3 provides the comparison of biodiesel and diesel properties [36]. Density and heating value affect the volume of fuel that will be used; viscosity, cetane number, cloud point, and pour point are important indicators for engine performance.

TABLE 3 Ranges of the specifications of the fuels used in the reviewed studies

Specification	Biodiesel	Diesel
Density(15°C)(kg/m^3)	870-895	810-860
Viscosity(40°C)(cSt)	3.5-5.5	2-3.5
Cetane number	45-65	40-55
Cold filter plugging point(°C)	-5 to 10	-25 to 0
Cloud point(°C)	-5 to 10	-20 to 0
Pour point (°C)	-15 to 10	-35 to 0
Lower heating value (MJ/kg)	36.5-38	42.5-44
Water content(mg/kg)	0-500	
Acid number (mg KOH/g)	0-0.60	
Ester content(% w/w)	>96	
Glycerin content (% w/w)	0-0.25	
Sulfur content (mg/kg)		15-500

- Cetane number (CN) is a prime indicator of fuel quality which is related to the ignition delay (ID) timing of diesel engines (the higher the CN, the shorter the ID time). Hexadecane ($C_{16}H_{34}$), a long straight-chain hydrocarbon, is the standard on the cetane scale with an assigned CN of 100. Generally, diesel engines run will with a CN from 40 to 55. For fuels with higher CN, the ID will be shorter, which means more time is provided for the combustion process to be completed. The CN increases with increasing chain length, and decreases with increasing unsaturation and branching. The influence of CN to NOx emissions is complicated. For diesel fuels, higher CN is correlated with reduced NOx emissions[37], especially for old, lower injection pressure engines [25]. With biodiesel, multiple conflicting effects will occur. On one hand, higher CN shortens ID and therefore increases NOx. This would be one explanation of higher NOx from biodiesels, because biodiesels usually have relatively higher CNs than diesel due to fatty acid compounds. On the other hand, higher CN lead to lower premixed combustion and softer changes in pressure and temperature, which decrease NOx [38].

- The low temperature flow properties (higher cloud point and pour point) are the major problems with biodiesel use in cold weather. The cloud point of a fluid is the temperature at which dissolved solids are no longer completely soluble. These solids begin to precipitate, giving the fluid a cloudy appearance. When temperatures reach the fuel cloud point, solids and crystals grow rapidly and agglomerate, which can clog fuel lines and

filters, and cause operability problems. When temperatures fall lower than the pour point (the lowest temperature at which it will pour or flow under prescribed conditions), the fuel is not pumpable. Usually, saturated fatty compounds have higher melting points than the unsaturated acids and are more susceptible to clogging problems.

- Viscosity is used to describe a fluid's resistance to flow. It affects the atomization of a fuel upon injection into the combustion chamber, which leads to incomplete combustion and formation of carbon deposits in the engine. The high viscosity of neat vegetable oil is the major reason why it can not be used as an alternative to diesel fuel. After transesterification, the viscosity of biodiesel is lower than that of the parent oil, but still higher than that of diesel. Viscosity increases with chain length and with increasing degree of saturation [25]. The higher viscosity of biodiesel may also affect the engine brake effective power, especially in full-load conditions due to decreased combustion efficiency [36].

- Biodiesel has approximately 9% less heating value per volume than conventional diesel fuel, resulting in significant power loss of biodiesel. As biodiesel has a higher density than diesel fuel, the fuel consumption (by volume) of biodiesel is higher than that of diesel if the engine efficiency (kg fuel/kW-hr) is the same.

- High lubricity of biodiesel reduces friction loss in engines and thus might improve the brake specific power [38].

Biodiesels from different sources have different fatty acid composition (chain length, degree of saturation). Therefore, cetane number varies, as does cloud point, melting point and viscosity. It is hypothesized that enriching neat biodiesel with certain fatty esters with desirable properties in the fuel can improve the properties of the whole fuel. To achieve a higher CN, we would prefer biodiesel with longer chains, and a higher degree of saturation, while optimizing for lower cloud point, pour point and viscosity would require biodiesel with a low degree of saturation. It is critical to balance these parameters when deciding which source is best, although production costs and availability are also important. Table 4 provides the composition of some common biodiesel sources [27].

TABLE 4 Fatty acid composition of some vegetable oils (%)

Vegetable Oil	Palmitic 16:0	Stearic 18:0	Palmitoleic 16:1	Oleic 18:1	Linoleic 18:2	Ricinic 12-OH-oleic	Other acids
Tallow	29.0	24.5	-	44.5	-	-	-
Coconut oil	5.0	3.0	-	6.0	-	-	65.0
Olive oil	14.6	-	-	75.4	10.0	-	-
Groundnut oil	8.5	6.0	-	51.6	26.0	-	-
Cotton oil	28.6	0.9	0.1	13.0	57.2	-	0.2
Corn oil	6.0	2.0	-	44.0	48.0	-	-
Soybean oil	11.0	2.0	-	20.0	64.0	-	3.0
Hazelnut kernel	4.9	2.6	0.2	81.4	10.5	-	0.3
Poppy Seed	12.6	4.0	0.1	22.3	60.2	-	0.8
Rapeseed	3.5	0.9	0.1	54.1	22.3	-	9.1
Safflower seed	7.3	1.9	0.1	13.5	77.0	-	0.2
Sunflower seed	6.4	2.9	0.1	17.7	72.8	-	0.1
Castor oil	-	3.0	3.0	3.0	1.2	89.5	0.3

Studies have shown that the use of biodiesel in diesel engines can improve emissions for PM, hydrocarbons and CO. The increase of NOx, however, is a big problem for the use of biodiesel. The chemical content of biodiesel is one essential reason for the NOx increase. Bakeas et al. [39] concluded that increased unsaturation, high value of glycerol content in the fuel, and the use of oxidized blends would lead to higher NOx emission.

The emissions from biodiesel are influenced by the source of biodiesel and the engine characteristics. With the use of different biodiesels and different engines, the emissions concentrations may vary significantly. Durbin et al. [30] compared the emissions of a California diesel fuel with neat biodiesel, an 80% California diesel/20% biodiesel blend, and a synthetic diesel fuel by operating them in four light heavy-duty diesel trucks. The neat biodiesel produced slightly higher NOx emissions and also produced higher PM emissions. This was attributed to the high organic carbon fractions in biodiesel (organic carbons were analyzed to be the primary constituents of the diesel particulate). In additional tests in 2007 [40], a California ultra-low sulfur diesel (ULSD) and different blends of two different yellow-grease biodiesels and one soy-based biodiesel were tested on various engines. The results showed that higher biodiesel blends had a tendency for higher THC and CO emissions on a 1992 F-9000 HD truck and lower PM emissions on the F-9000 and 2004 Humvee. Ilkilic and Aydin [41] found lower CO_2, CO, HC, smoke opacity and NOx emissions of B75 cotton seed oil based biodiesel operated on a compression ignition engine, although the specific fuel consumption of biodiesel blends was higher than that of diesel fuel by approximately 3%.

The sources of biodiesel can also affect engine performance. Bunting et al. [42] tested biodiesel blends derived from palm, coconut, rape, soy and mustard using an HCCI engine and found that improved performance (improved specific fuel consumption and thermal efficiency, and lower HC, smoke, and combustion variability) was provided by those fuels with lower cetane number and lower boiling points. Lin et al. [43] found that emulsified biosolution/soy-biodiesel/premium diesel fuel (PDF) blends prepared by nanotechnology had advantages in energy savings and in reducing the emissions of both

PM and polycyclic aromatic hydrocarbons (PAHs) from diesel engines as compared with PDF, soy-biodiesel/PDF blends, and emulsified soy-biodiesel/PDF blends.

The reasons for higher NOx emissions from biodiesel have also been investigated. Higher residence times inside the combustion chamber for biodiesel and higher concentrations of CH can both result in higher NOx emissions. In general, the best way to reduce NOx emissions is to decrease the temperature in the combustion chamber. Fang et al. [44] pointed out that maximum heat release rate can be reduced by retarding fuel injection, effectively reducing NOx emissions. In their study, different ratios of soy biodiesel blends were operated in traditional direct-injection diesel engines. The NOx production of B20 (20 vol % soybiodiesel and 80 vol % European low-sulfur diesel), B50, and B100 in late-injection strategies were 68.1%, 66.7%, and 64.4% lower respectively, than pure European low-sulfur diesel. Qi et al. [45] also proved that a retarded injection time could decrease NOx emission, and that the NOx level can also be reduced with the use of Exhaust Gas Recirculation.

Additives are another way to improve engine performance, and reduce NOx. Kannan et al. [46] used ferric chloride as a fuel borne catalyst for waste cooking palm oil based biodiesel, and found that the additive resulted in a decreased brake specific fuel consumption of 8.6%, while the brake thermal efficiency increased by 6.3%. Lower nitric oxide emissions were also produced when the ferric chloride was added to biodiesel. Torres-Jimenez et al. [47] added bioethanol in rapeseed oil based biodiesel, and found that the addition of bioethanol reduced fueling, injection time, injection duration, mean injection rate and maximum injection pressure and increased injection delay compared to

pure biodiesel. All of these effects made the biodiesel injection characteristics closer to the diesel fuel injection characteristics, and are expected to decrease biodiesel NOx emissions. Anand, Sharma, and Mehta [48] tested neat karanji oil derived biodiesel and diesel-methanol blends under constant speed and varying load conditions without altering injection timings. The results indicated that for biodiesel-methanol blends the ignition delay was higher, while a shorter combustion duration was observed compared to neat biodiesel fuel. Due to the methanol addition, there was also a thermal efficiency increase, with the maximum value of 4.2% at 80% load and 16.67s^{-1} engine speed. The emissions of NOx and PM were significantly lower with the biodiesel-methanol blends.

Chapter 2

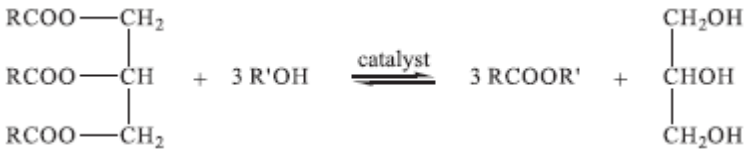
Method and Experiment Setup

In order to investigate the effect of biodiesel composition on engine emissions, seven biodiesels from different sources were produced and their components identified by CNH analysis and GC-MS. Then the biodiesels were combusted in a single cylinder engine with different engine loads. PM was collected with a 13-stage impactor, and gas emissions of CO_2, CO, HC, NO and NO_2 were analyzed by Semtech-DC analyzer. All of the biodiesel emission results were compared with the emissions from ULSD.

2.1 Fuel production

In this study, used canola, high-erucic acid rapeseed (HEAR), olive, palm, coconut, canola, and soybean oil were utilized as feedstock. Vegetable oils are triglycerides, containing three chains of fatty acids connected together by a glycerin molecule [49]. Generally, large molecules such as triglycerides have high viscosity and low volatility, which can adversely affect engine performance. Therefore, a process called transesterification is used to break down these molecules. In the transesterification process, alcohol (usually ethanol or methanol) reacts with triglyceride, and form biodiesel (fatty acids) and byproduct (glycerol). The transesterification reaction is show below: 1mol of triglyceride reacts with 3mol of alcohol and gives 3mol of fatty acids and 1mol of glycerol. The reaction can be catalyzed by both acid and alkaline catalysts. Most

commonly, base-catalyzed transesterification is employed to treat vegetable oil feedstock as it is the most economical process.



For this study, biodiesels were prepared by students working for the KU Biodiesel Initiative under Dr. Susan Williams. First, each vegetable oil was reacted with methanol with a 6:1 molar ratio of methanol to oil, then 1% sodium methoxide was added as a catalyst, based on the mass of the oil. The mixture was then reacted for four hours with mechanical stirring at a temperature of 333.15K. At least 12 hours was then allowed for the resulting biodiesel and glycerol mixture to separate. Next, the denser glycerol was removed, and the biodiesel was washed three times to remove redundant methanol, soap (a side-reaction product), and impurities. Finally, water was removed by spray drying the biodiesel for four hours.

2.2 Biodiesel composition analysis

1. CHN analysis

All of the biodiesels were sent for analysis to Micro Analysis Inc. (Wilmington, DE), in order to determine the weight (by percent) of carbon, hydrogen, and nitrogen contained in the biodiesels. In the tests, the samples were combusted in a pure oxygen

environment; gaseous CO_2, H_2O and N_2 produced were separated and detected by thermal conductivity based on Pregl and Dumas methods (ASTM D5291).

2. Gas chromatography-mass spectrometry (GC-MS) analysis

GC-MS is a common analytical technique for the detection and quantification of fatty acid composition in biodiesel. The GC-MS is composed of two major building blocks: the gas chromatograph and the mass spectrometer.

Chromatography is a physical separation method. First the sample is vaporized and carried by a carrier gas (mobile gas phase) through a column: usually the carrier gas is an inert gas such as helium or an unreactive gas such as nitrogen, and the column is a piece of glass or metal tubing. Inside the column is a microscopic layer of liquid or polymer called the stationary bed (stationary phase). Samples equilibrate into the stationary liquid phase based on their solubilities at the given temperature. Because the components of the sample have different relative vapor pressures and affinities for the stationary bed, each component exits the end of the column at a different time (retention time), and can be detected identically [50]. However, the GC system cannot confirm the identity or the structure of the peaks. Therefore, an MS is needed.

MS is an analytical technique for determining masses of particles that can be used to elucidate the chemical structures of molecules. The separated components from the GC are sent into an ionization source to be ionized (usually by impact of a highly energetic electron beam (~70eV), forming charged particles (ions), which further fragment to yield predictable patterns. Finally, the intact ions and fragments pass into the mass

spectrometer's analyzer (separated by electromagnetic fields according to their mass-to-charge ratio), and are detected [50].

In this study, an Agilent 6890 Series GC system and an Agilent 5973 Network Mass Selective Detector were used, and the data were collected and analyzed using Agilent G1701EA GC/MSD Chemstation Software. The column was an Agilent (model 19091N-231 HP-INNOWax) polyethylene glycol capillary column, which is capable of separating methyl esters ranging from methyl hexanoate (C6:0) to methyl lignocerate (C24:0). The Internal Standard method was used for quantitative analysis. A fatty acid methyl ester (FAME) C8-C24 mix from Supelco was used as a standard to calculate the response factor of each fatty acid, and an ethyl stearate with a concentration of 2µg/ml was used as an internal standard. The calculation equations are below.

$$\text{RF} = \frac{A_s}{A_{is}} \times \frac{C_{is}}{C_s}$$

Where:

RF = response factor

A_s = peak area or height of analyte

A_{is} = peak area or height of the internal standard

C_s = concentration of the analyte

C_{is} = concentration of the internal standard

For each fatty acid, the response factor was calculated using a standard FAME mix. This response factor was then used to calculate the concentration of the specified fatty acid in the sample by the following equation.

$$\text{Concentration} = \frac{A_s \times C_{is} \times D}{A_{is} \times RF}$$

Where D = dilution factor

Biodiesel samples were first diluted 5000 times with hexane, and then 2mL of this mixture was put into GC auto sampler vials in ready of analysis. For each run, 1mL of sample was injected into the GC. The GC was programmed to stay at 120°C for 1 min, then the temperature increased at 6°C/min to 180°C, 1.5°C/min to 198°C, 5°C/min to 228°C and then held at 228°C for 5min. The injection port and transfer line were held at 250°C. Helium was used as the carrier gas with a flow rate of 1.4mL/min. In MS, 70eV was used for electron ionization. The temperature of the ion source was 230°C and the quadruple temperature was 150°C [51]. With the result spreadsheets provided by Chemstation Software, concentrations of different fatty acids in biodiesels were calculated according to the equations above.

2.3 Engine test

Engine test studies were performed in conjunction with students in Dr. Christopher Depcik's Research Group in Mechanical Engineering. A Yanmar L100V direct-injected diesel engine, which is a single cylinder diesel engine, was used for the

engine tests. This engine provided better configurations of fluid dynamics and heat transfer related to combustion than multi-cylinder engines. A constant engine speed of 3600 rotations per minute (RPM) is kept using a mechanical fuel pump-line-injector. Injection occurs at 15.5±0.5° before piston top-dead-center with a pressure of 19.6MPa. A NorthStar electric generator coupled to the crankshaft is employed to provide different engine loads. Resistance heaters can supply variable electrical loading and selection of the specific power of these heaters allows selection of different engine loads. Details of the engine and generator are showed in Table 5. A FUTEK rotary torque-sensor (model #TRS-705) is connected between the engine and generator shafts to provide accurate torque values, and a Merriam laminar flow element (model #50MW20-2) and an Omega differentia pressure transducer (model #PX 277-30D5V) are used to measure the engine intake airflow.

TABLE 5 Engine and generator specifications [52]

Engine	Value
Manufacturer and Model	Yanmar L100V
Type	Vertical Direct-Injection Compression Ignition
Engine Intake	Naturally Aspirated
Cooling	Air-Cooled
Cycle	4-Stroke
Displacement	435 cc
Number of Cylinders	1
Number of Valves	1 Intake, 1 Exhaust
Bore	86mm
Stroke	75mm
Compression Ratio	21.2
Injection Timing	15.5 (+/- 0.5) degrees BTDC
Continuous Rated Output	8.3 hp SAE
	6.2 kW
Rated Speed	3600 RPM
Injector Pressure	19.6 MPa
Aftertreatment	None
Engine Oil Used	Shell 15W-40
Generator	
Manufacturer and Model	NorthStar 5500BDG
Maximum Output	5500 W
Continuous Output	5000 W
Voltage	120/240 V
Phase	Single-phase (4-wire)
Frequency	59.0-62.0 Hz
Power Factor	100%
Allowable Current (120V/240V)	2@20 Amp/ 1@20 Amp

Each of the fuels were tested for five loadings, which were approximately 0%, 25%, 50%, 75%, and 100% of the generator rated output. The rated continuous generator power is 80% of the rated continuous engine power. The engine exhaust temperature was monitored 892mm downstream of the exhaust port. When the change of engine exhaust temperature was less than 1% in a minute, the engine was considered to be at steady-state

operation, at which point engine performance and emissions data were collected. A National Instruments hardware system was employed to record engine performance data at a sample rate of ten samples per second for two minutes during the emissions tests. Additional details of the experimental setup are available in Michael Mangus's thesis [53].

2.4 Emission analysis

A Semtech-DS mobile Emissions Analyzer was used for gas emissions data collection at a sampling rate of one sample per second for ten minutes. The Semtech product line is based on stand-along measurement subsystems. A heated Flame Ionization Detector (FID) is used for total hydrocarbon (THC) measurement; a Non-Dispersive Ultraviolet (NDUV) analyzer is used for nitric oxide (NO) and nitrogen dioxide (NO_2) measurement; and a Non-Dispersive Infrared (NDIR) analyzer is used for carbon monoxide (CO) and carbon dioxide (CO_2) measurement. An auxiliary electrochemical sensor is used for oxygen (O_2) measurement. In order to calculate the exhaust mass emissions, the SEMTECH EFM electronic exhaust flow meter (Micro-Motion Coriolis flow meter, model #CMF010M) was used to accurately measure the engine exhaust flow. In addition, temperature, pressure and humidity sensors were used to monitor the ambient environment and exhaust gas. The humidity is important because it can substantially influence NOx emissions. A humidity correction (Kh), is calculated by the SEMTECH software using method CFR40 §86.1342-94 or CFR40 §1370-2007 [54]. The Post-Processor application software was used to calculate exhaust mass emissions for all

measured exhaust gases. Gas emissions data were collected for all of the fuels under all loads.

In order to get accurate emission data, zero/span/audit processes were carried out daily. The sampler was zeroed to ambient air as a baseline, with span and audit bottles used to calibrate the high end and middle of the calibration range. In the middle of tests, the Semtech was zeroed every hour to make sure the baseline did not shift. At the end of every testing day, a re-audit was performed to make sure that the data collected meet all accuracy requirements. The calibration gas bottles and the THC FID fuel bottle were provided by Scott Gas Company.

In addition to gas emissions, PM for each fuel was collected at 25% load for one hour using a Dekati Low-Pressure Impactor (DLPI). The DLPI is a 13-stage cascade impactor for measuring gravimetric particle size distribution. Each stage consists of a plate with nozzles in it (jet plate, up) and a plate with a filter to collect particles (impaction plate, down). After the exhaust passes through the nozzles at high speed, it makes a sharp turn between the two plates, leaving particles larger than a certain size collected in the filter. The DLPI can collect particles from 10 microns down to 30 nm size nominal diameter. Table 6 provides the cut size for every stage defined as the size of particles collected with 50% efficiency. Prior to sampling, 25mm polycarbonate foils were sprayed with grease (Apiezon-L grease dissolved in hexane) to avoid particle bounce. After staying at a constant temperature of 25°C and a relative humidity of 40% for 24 hours, filters were weighed on an electronic microbalance prior to use. During sampling, a Sogevac Leybold vacuum pump induced a flow rate of 10 liters per minute

through the collection system. The total sampling time was one hour. After sampling, the filters were removed from each stage and placed under constant temperature and humidity again before a second weighing. The differences between the two measurements are the mass of PM collected on each stage. The 25% load was chosen because it produced the most significant PM levels. At 0% load, a lean fuel-to-air mixture in the engine won't create excessive PM, and at loads above 25%, high pressure and temperature in the cylinder lead to better combustion and, therefore, low PM levels.

TABLE 6 Nominal value for Impactor filter stages

Stage	D50% (μm)
13	10
12	6.8
11	4.4
10	2.5
9	1.6
8	1.0
7	0.65
6	0.40
5	0.26
4	0.17
3	0.108
2	0.060
1	0.030

2.5 Statistical analysis

Statistical analyses were carried out to examine the correlations between biodiesel chemical properties/composition and individual emissions components. Analysis of variance (ANOVA) and Pearson's correlation were the two methods used in our study, using Minitab and Microsoft Excel, respectively.

ANOVA is an extremely important test in statistics which is widely used in the analysis of experimental data. The ANOVA test is used to determine if means of more than two groups are equal. The test is based on F-distribution function. In our study, we used a significance level of 5% (95% confidence) and we regarded two groups of data as statistically significantly related when a p-value was less than 5%.

In order to further explore the relationship between biodiesel composition (fatty acids chain length, saturation degree) and NOx emissions, Pearson's correlation coefficients, which is defined as the covariance of the two variables divided by the product of their standard deviations, were calculated. Coefficients of "1" or "-1" mean that the two variables are exactly linear related, and a "0" implies there's no linear correlation at all between variables.

2.6 Biodiesel truck road test

After the tests in the engine cell, the next step in fuel testing is to conduct on-road tests to get real-world emissions data. For this study, several demonstration tests were

conducted to establish an on-road method. A 2005 Dodge Ram with a V8 5.7L/350 engine was driven around campus and on the highway while burning biodiesel. Waste cooking oils collected from university dining halls were used to produce biodiesel for these tests. The Semtech was placed on the back seat of the truck and the heated sample line was fed through the back window. Clamps were used to fix the sample line on one side of the truck until it reached the end of the tailpipe. The flow meter used in engine tests was too small for the truck tailpipe, so an Aux Temp Sensor was attached to biodiesel pipe tail for emissions monitoring instead. With this method, emissions concentrations are recorded, but the total emissions mass couldn't be calculated. Before every test, the Semtech was warmed up and calibrated on campus using wall power. For sampling, we changed the power to a set of two storage batteries (12V) to support on-road tests. The batteries were wired in parallel to insure that the Semtech lasted enough time to complete the tests.

Tests were carried out several times on different days. First, we drove around campus and downtown in Lawrence, and found out that emission data changed so much along the route that it was meaningless to record emission data solely without engine information. Then we tried to involve the Semtech Vehicle Interface during the tests to monitor engine data, as well as emission data (engine speed, vehicle speed, engine load, and throttle position). Meantime, in order to get steady data for some tests, we started testing on the highway, where we could avoid significant speed changes and sudden stop. However, we failed to get torque data using the protocol software for light-duty truck and therefore still couldn't do full emissions analysis. Finally, we decided to use a global positioning system to get road information (latitude, longitude, altitude, ground speed) in

the tests, and recorded three different tests: randomly driving in the downtown area and on the highways (K-10 state highway, east of Lawrence) at certain speeds set by cruise control (55mph and 65mph).

Chapter 3

Results and Discussion

Some of the results in this chapter were previously published in Energy & Fuels[52]. Sections 3.1 and 3.2 contain significant experimental and analytical contributions from the other co-authors of that paper, particularly Michael Mangus of the Department of Mechanical Engineering. Sections 3.3 and 3.4 contain elements published in that paper but developed more extensively for this thesis.

3.1 Biodiesel chemical analysis

Table 7 below summarizes chemical properties of all fuels in this research. Compared with ULSD, all of the biodiesels had higher H:C molar ratio, higher oxygen content, slightly higher density, larger kinematic viscosity, and smaller energy content. H:C ratios of biodiesels varied from 1.85 to 2.02. Used cooking oil, canola oil and soybean oil was less saturated than the other biodiesels, and coconut oil was the most saturated one of all. The average oxygen content of biodiesels was 10.75%, and the oxygen content of coconut was 14.44%, which was significantly higher than the rest. The densities of biodiesels showed little difference, with an average value of 873.08 kg/m^3. Compared to ULSD, all of the biodiesels had higher viscosity, varying from 2.72 cSt to 8.19 cSt. Coconut oil had the nearest value to ULSD. For the energy content, the average value of biodiesels was 87.1% of ULSD per weight. Considering the higher density of

biodiesels, the average energy content by volume was 90.6% of ULSD. Rapeseed oil had the highest energy content and the coconut oil had the lowest value. As mentioned in Chapter 2.1, in the process of biodiesel production, glycerol is formed as a byproduct, which needs to be separated and removed. In ASTM D6584-10a which is used to measure glycerol in the fuel, rapeseed oil failed. Since that the result was not far away from the test criteria, we still include rapeseed oil in our result part.

TABLE 7 Chemical properties of ULSD and seven biodiesels

Sample	H:C	Oxygen content (%wt)	Density (kg/m^3)	Kinematic Viscosity (cSt)	Energy Content (kJ/kg)
ULSD	1.81	0.09±0.3	839.6	2.48 ±0.001	45494
Used Cooking Oil	1.85	10.47±0.3	882.69	6.56 ±0.001	39663
Rapeseed Oil	1.9	9.37±0.3	877.43	8.19 ±0.013	40352
Olive Oil	1.9	10.36±0.3	870.03	4.64 ±0.002	39550
Palm Oil	1.97	11.12±0.3	866.26	4.64 ±0.001	39825
Coconut Oil	2.02	14.44±0.3	865.52	2.72 ±0.002	38228
Canola Oil	1.88	9.64±0.3	875.58	4.04 ±0.002	39869
Soybean Oil	1.88	9.85±0.3	874.08	3.69 ±0.001	39880

Table 8 presents the concentration ratios of different fatty acids in every biodiesel based on GC-MS analysis (ex. C18:1 means the fatty acid has a chain of eighteen carbons, and has one double-bond in it). It is easy to see that biodiesels from different feedstocks had quite different components, both in fatty acids chain length and saturation degree. Coconut oil had more short chains fatty acids than any other fuel. The total concentration

of C10, C12 and C14 acids for coconut oil was > 78%. Palm oil had more than 40% of C16 and more than 50% of C18. Used cooking oil, olive oil, canola oil and soybean oil had around 90% C18 compounds, while rapeseed oil had more long chain of fatty acids (56% C22). Based on these results, 90% of fatty acids in coconut oil were saturated, making it the most saturated oil, followed by palm oil, whose components were mostly saturated fatty acids and single double-bond fatty acids. Soybean oil was the one least saturated, with more than 60% of fatty acids having multiple double-bonds.

TABLE 8 Concentration ratios (weight %) of fatty acids in biodiesels

Synonym	Used Cooking Oil	Rapeseed Oil	Olive Oil	Palm Oil	Coconut Oil	Canola Oil	Soybean Oil
C10:0	-	-	-	-	6.5	-	-
C12:0	-	-	-	0.60	52	-	0.19
C14:0	0.14	-	-	1.1	20	-	0.12
C16:0	6.6	2.9	8.2	41	9.1	4.0	10
C16:1	0.20	-	0.37	0.17	-	0.16	-
C18:0	2.3	1.0	3.4	4.3	2.6	1.8	3.9
C18:1	56	17	71	43	7.7	65	25
C18:2	25	11	15	9.5	1.8	21	54
C18:3	8.0	11	1.1	-	-	8.1	6.3
C20:0	0.62	0.65	0.35	0.33	-	0.47	0.21
C22:0	0.51	0.52	0.52	-	-	0.23	0.31
C22:1	-	56	-	-	-	-	-
Saturation%	10.17	5.07	12.47	47.33	90.2	6.5	14.73
Single double-bond	56.2	73	71.37	43.17	7.7	65.16	25
Poly double-bonds	33	22	16.1	9.5	1.8	29.1	60.3

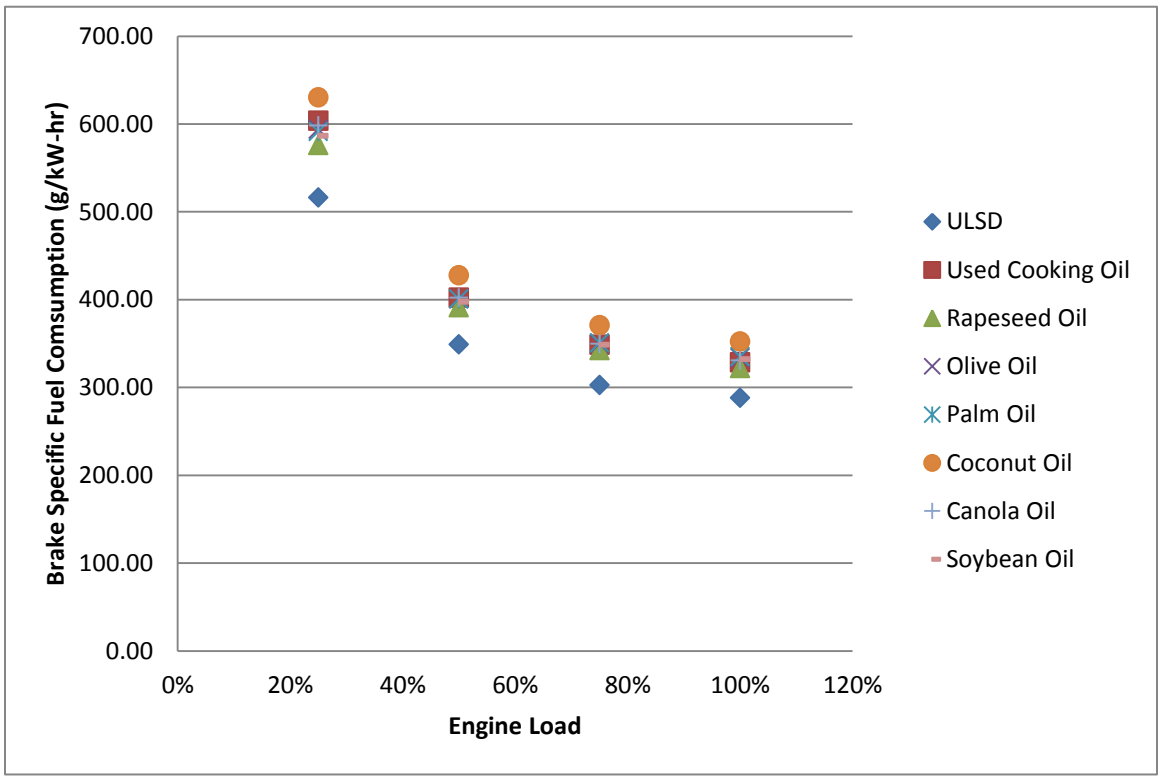
Comparing our results of biodiesels composition in Table 8 with Table 4 in Chapter 1, it appears that the compositions of olive oil, coconut oil and soybean oil are almost the same, except our rapeseed oil has more long chain fatty acids (C22). Also,

Fassinou et al. [55] tested and summarized fatty acids composition of 38 different vegetable oils, fats and biodiesels, in which biodiesels from waste cooking oil, rapeseed oil, olive oil, and soybean oil were analyzed. In their research biodiesel from rapeseed oil had 23% of C22:1 while ours has 56%. However, Graboski and McCormick pointed out that biodiesel from some rapeseed oil sources has 50%-60% of C22:1 [56].

3.2 Gaseous emissions from biodiesels compared with ULSD

Because of the lower energy content in biodiesels, fuel consumptions for all biodiesels are higher than with ULSD. Figure 4 shows the brake specific fuel consumption (BSFC) of biodiesels compared with ULSD at different loads (25%, 50%, 75% and 100%). BSFC is calculated by using the rate of fuel consumption divided by the power produced, which is a good parameter to compare fuel efficiency. Among the seven biodiesels, rapeseed oil had the lowest BSFC, however, it was still 12% higher than ULSD; coconut oil had the highest BSFC, with more than 22% higher than ULSD. Since the engine is tuned to have best performance at high loads, BSFC decreased with the increased engine load due to higher increases in brake power compared to fuel consumption. The situation of 0% load was not an actual zero but somewhere close to it, which was hard to control during the data recording period, so the 0% data of it was not included here. However, the difference in fuel efficiency between biodiesel and ULSD is even more significant at 0% load.

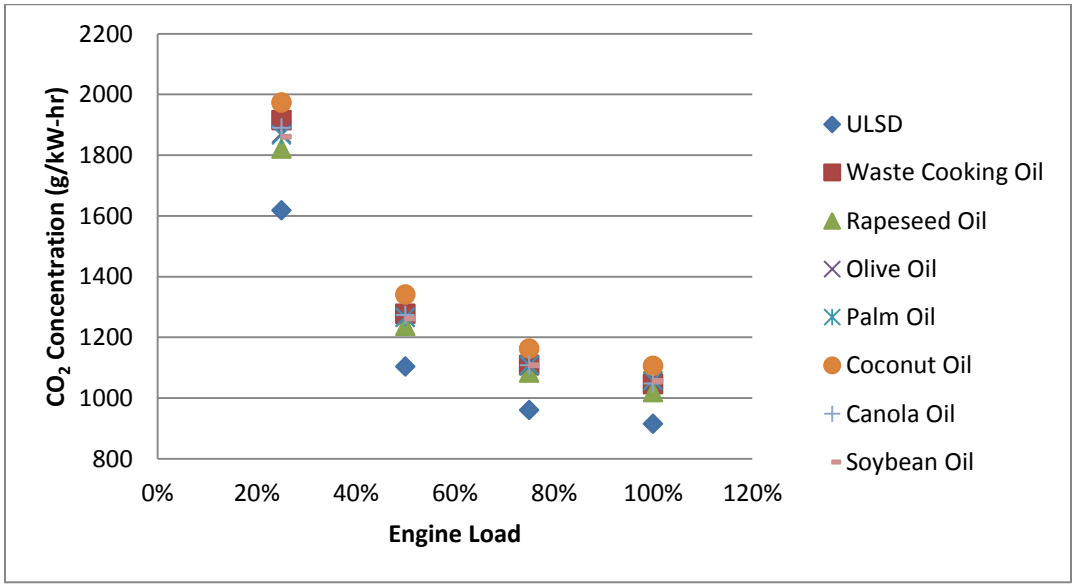
Figure 4 Brake specific fuel consumptions of ULSD and biodiesels



In this study, gaseous emissions were measured in parts per million (HC, NO, NO_2) or percent by volume (CO_2 and CO) by the Semtech-DS. There are two ways to compare emission concentrations, in the units of gram emission per fuel weight (g/kg fuel) or gram emission per unit power. We used brake specific emissions (g/kw-hr) to compare the performance of biodiesels with ULSD. Brake specific emissions are the mass flow rate of emissions per unit power output, which is a better indicator since it takes fuel efficiency into account. Figures 5-10 presents gaseous emissions concentrations from biodiesels compared with ULSD under different loads. Again, data for 0% load are not included. As previously mentioned, our engine performed most efficiently at higher load, resulting in lower break specific emissions of all constituent as the load increasing.

The productions of CO_2 from all fuels were almost similar. With the increase of engine load, the fuels are burned more completely, and slightly more CO_2 are formed per weight fuel. At low loads (0% and 25%), ULSD produced less CO_2 than biodiesels per mass, however at mid and high loads, most of the biodiesels produced less CO_2, expect waste cooking oil and soybean oil. When the brake specific CO_2 calculated as shown in Figure 5, it is apparent that CO_2 from biodiesels were higher compared with ULSD, and the degree of difference decreased with the increase of load. Generally, the trends showing from Figure 5 look like those from Figure 4. Biodiesels produced 12% (rapeseed oil) -21% (coconut oil) more CO_2 than ULSD.

Figure 5 CO_2 from ULSD and biodiesels



CO and HC both result from partial combustion of the fuel. When engine load increases, fuels are burned more completely under higher temperature and pressure, and therefore CO and HC emissions decrease (Figure 6 and Figure 7). Comparing emissions

from 25% load and 100% load, the specific brake emissions of CO had a reduction of 82% for ULSD, and 67%(coconut oil)-75% (olive oil and soybean oil) reductions for biodiesels. All biodiesels produced less CO than ULSD at low loads. The reduction of CO from biodiesels was mainly because of high oxygen content and low carbon content in biodiesels, as well as the advanced injection. Some biodiesels started to produce more CO than ULSD above 50% load. Soybean oil, palm oil and olive oil always performed better than ULSD, while coconut oil and canola oil produced 40% more CO than ULSD at 100% load. However, CO emissions were generally low at high loads for all fuels. This might be the reason for not seeing CO reduction from biodiesels. HC emissions from all fuels were low, and with the increase of load from 25% to 100%, up to 83% reduction of HC could be seen from all fuels. Biodiesels produced less HC than ULSD, with the exception of coconut oil. Published research has shown that biodiesels with long chain length and high saturation can produce a high reduction of HC emissions [57].

It is interesting to notice that coconut oil produced the most CO and HC among all fuels, while it produced the least PM, the other incomplete combustion production. In fact, coconut oil was very different from other fuels: it had much higher oxygen content than others; it had more than 90% of saturated fatty acids making it the most saturated fuel in our study; the fatty acids chain length in it was shorter; and the energy content of it was the lowest of all. In addition, shorter chain length and high saturation degree resulted in a high CN for the coconut oil. These factors (along with the high oxygen content and advanced injection timing) would predict big reductions in CO and HC emissions from coconut. However, these effects were not observed. We should say that the low energy content was one of the reasons making it having highest CO and HC,

because we were comparing the emissions in the unit of g/kW-hr, however, coconut oil performance on CO and HC was still not good when we changed the unit into g/kg fuel. The small compound structure might be the reason for high gas emissions and low PM for coconut oil.

Figure 6 CO from ULSD and biodiesels

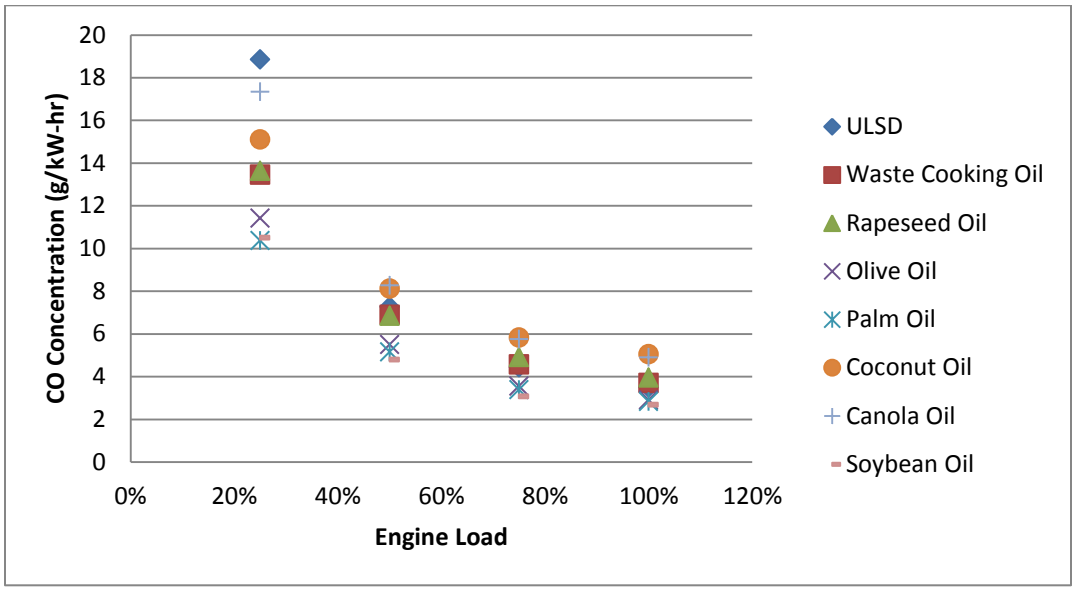
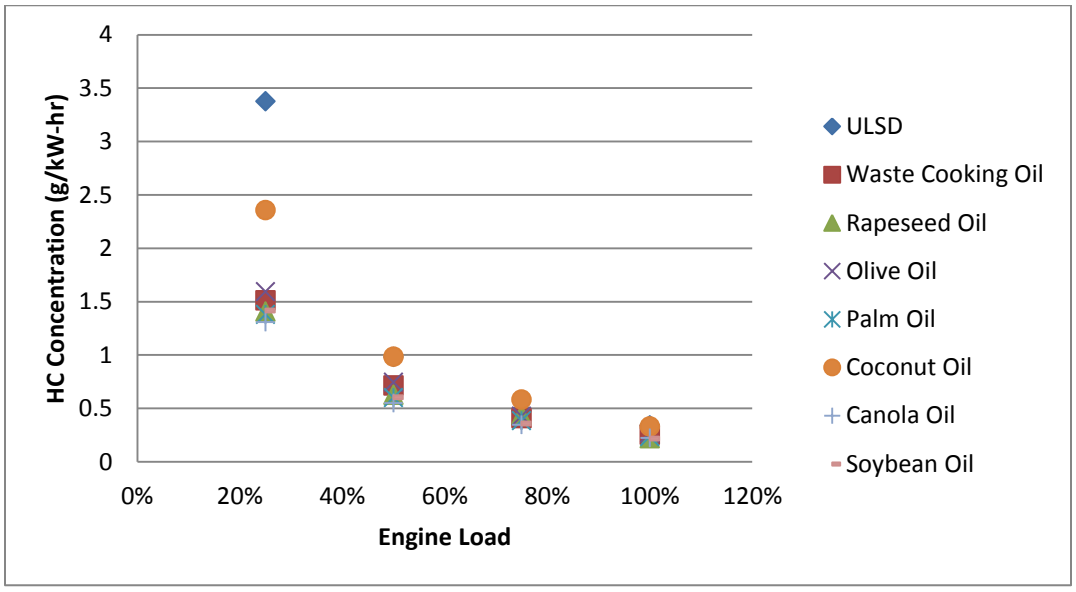


Figure 7 HC from ULSD and biodiesels



The specific emissions of NO and NO_2 both decreased with increased engine loads. All biodiesels produced more NO than ULSD at 0% and 25% load, due to advanced injection and additional oxygen content. Coconut oil and palm oil started to show less NO than ULSD at 50% load, followed by more biodiesels showing less NO at higher loads. Rapeseed oil, waste cooking oil and soybean oil always produced more NO than ULSD. Biodiesels with more long chain and unsaturated fatty acids (waste cooking oil, soybean oil and rapeseed oil) produced higher NO emissions. Coconut oil had the shortest chain fatty acids, as well as the highest degree of saturation. However, it produced more NO than palm oil, maybe because of its extremely high oxygen content. NO_2 forms from the further oxidation of NO, but converts back to NO when the temperature was extremely high. With the use of biodiesels, in-cylinder temperature was high due to advanced injection, and all biodiesels produced less NO_2 than ULSD at all loads. When comparing biodiesels, NO_2 emissions decreased with saturation degree and

increased chain length, resulting in coconut oil and waste cooking oil producing more NO_2 than other biodiesels. The superiority of biodiesels in NO_2 production was more significant at high load. Overall, waste cooking oil produced the most NOx and palm oil produces the least. ULSD had the highest NO_2/NOx ratio of all fuels, followed by coconut oil and waste cooking oil. The ratio of NO_2/NOx for every fuel decreased when the load increased. The average ratio is 24% at 25% load, falling down to 5% at 100% load. This also showed that NO is the majority of total NOx under all conditions.

According to numerous references [58-60], NOx emissions depend on many factors, including engine type, duty cylinder, fuel injection, biodiesel source, and others. Because of all these factors, there is not a complete understanding of NOx formation, although there are multiple models and theories to explain the increased NOx formation from biodiesels. The most common explanation is that biodiesels produce more NOx than ULSD due to higher cylinder temperature, which is a result of both maximum temperature and duration of combustion time. This is based on the assumption that thermal NOx is dominant. However, in our test, some biodiesel, especially palm oil, had better performance for NOx production than ULSD. There was also other research showing lower NOx from biodiesels [61-63]. The major explanation was low chamber temperature although none of these studies measured it directly (one did find lower emissions temperature when biodiesel was used). When we have a look at the NOx emissions per mass fuel (Figure 10(b)), it can be found that all fuels produce most NOx at 50% or 75% load, but not 100% load, which may be indicates that chamber temperature is not the only factor influencing NOx in our test.

Figure 8 NO from ULSD and biodiesels

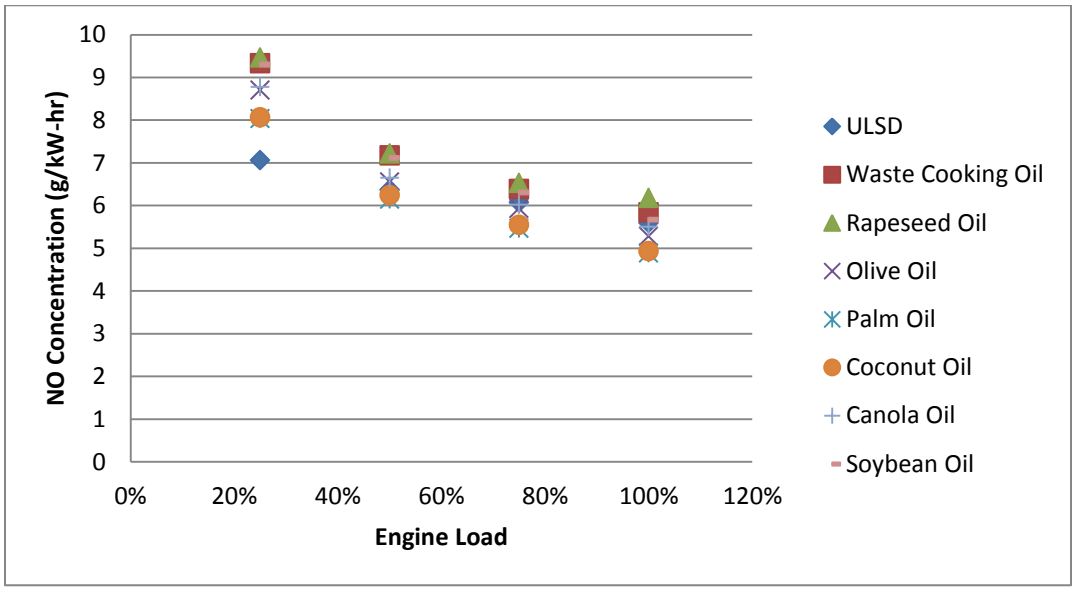


Figure 9 NO_2 from ULSD and biodiesels

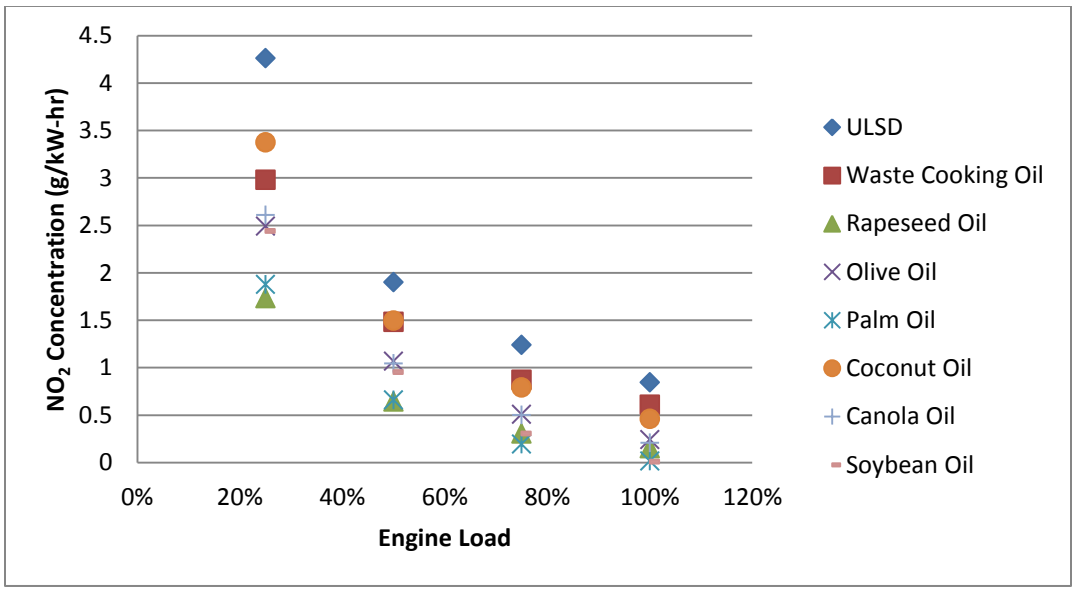


Figure 10(a) NOx from ULSD and biodiesels (g/kW-hr)

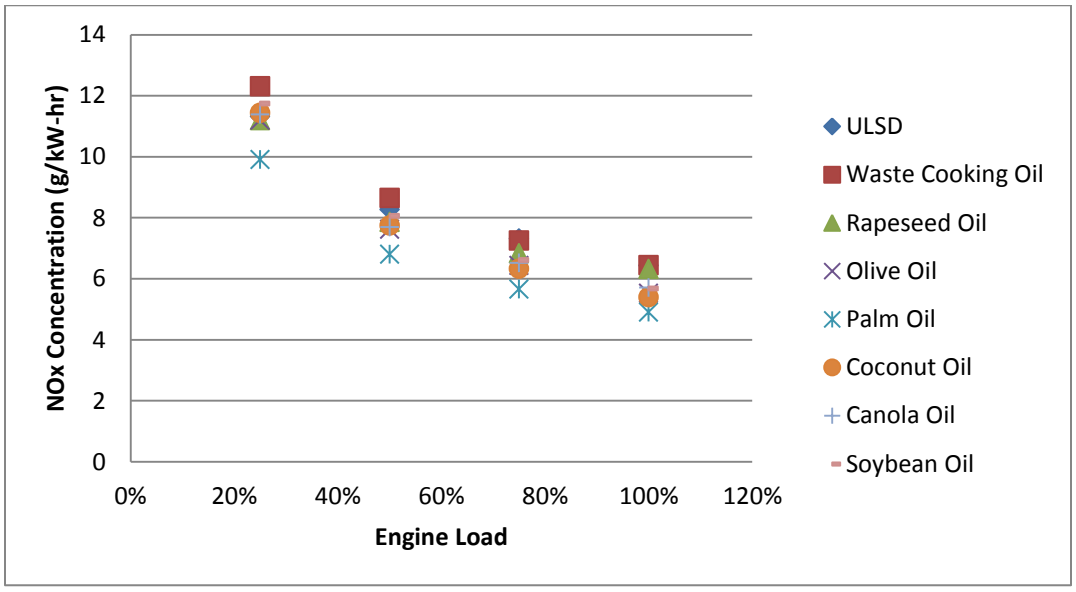
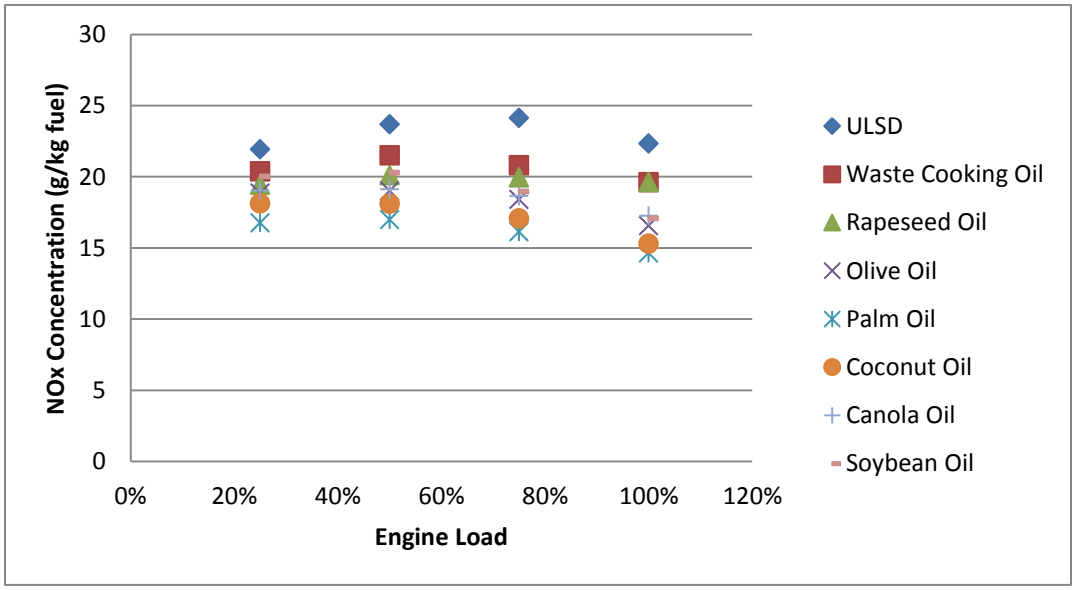


Figure 10(b) NOx from ULSD and biodiesels (g/kg fuel)



3.3 PM reduction from biodiesels

According to Heywood [64], there are three main components in PM: dry soot, soluble organic fraction and sulfate. Usually, the sulfur content in biodiesel is low (10-15ppm) and can be mostly ignored. This is also true with ULSD, which contains less than 50ppm sulfur. In our study, the PM filters stayed in a drying chamber for over 24 hours after collection, so the PM results here are primarily for dry soot. Usually, petroleum derived diesel contains 20-40% (vol%) aromatic hydrocarbons which is a big cause of soot, while biodiesel has almost no aromatic content. Additionally, biodiesel has about 10% of oxygen content. With the absent of aromatic components and the high oxygen content, biodiesels should produce much less PM than ULSD. Finally, advances in fuel injection timing when using biodiesels resulting in longer residence times of soot particles at high temperatures. This promotes PM oxidation, causing additional reductions in emissions levels.

The PM from ULSD and seven biodiesels were collected by DLPI. From Figure 3, PM_{10} and $PM_{2.5}$ from each fuel can be seen, as well as ultrafine particle (UFPs) content. UFPs are particles with diameter less than 100 nanometers, much smaller than PM_{10} and $PM_{2.5}$. UFPs can deposit in lungs, and from there can be absorbed into bloodstream. While there's no regulation for this size of particles for ambient air pollution, EPA might regulate it in the future. It was clear that all biodiesels had significant reductions of PM compared with ULSD, and that $PM_{2.5}$ contributed to the majority of total amount of PM for all fuels. $PM_{2.5}$ from olive oil had the smallest ratio of all, which was 76.6%, followed

by palm oil, whose $PM_{2.5}$ was 84.0% of total PM. $PM_{2.5}$ of canola oil had the highest ratio of 98.5%. In $PM_{2.5}$, UFPs accounted for more than 50% from all fuels except waste cooking oil. Table 9 calculated the reductions of PM_{10} and $PM_{2.5}$ by using biodiesels compared with ULSD. Generally, the values of PM_{10} and $PM_{2.5}$ reduction were similar, except olive oil and palm oil, whose $PM_{2.5}$ reductions were higher. Coconut oil produced the largest PM reduction of all, while waste cooking oil produced the smallest PM reduction. The PM level was highly related to the degree of fuel combustion: the more completely the fuel combusted, the less PM was formed.

Figure 3 PM from ULSD and biodiesels (mg)

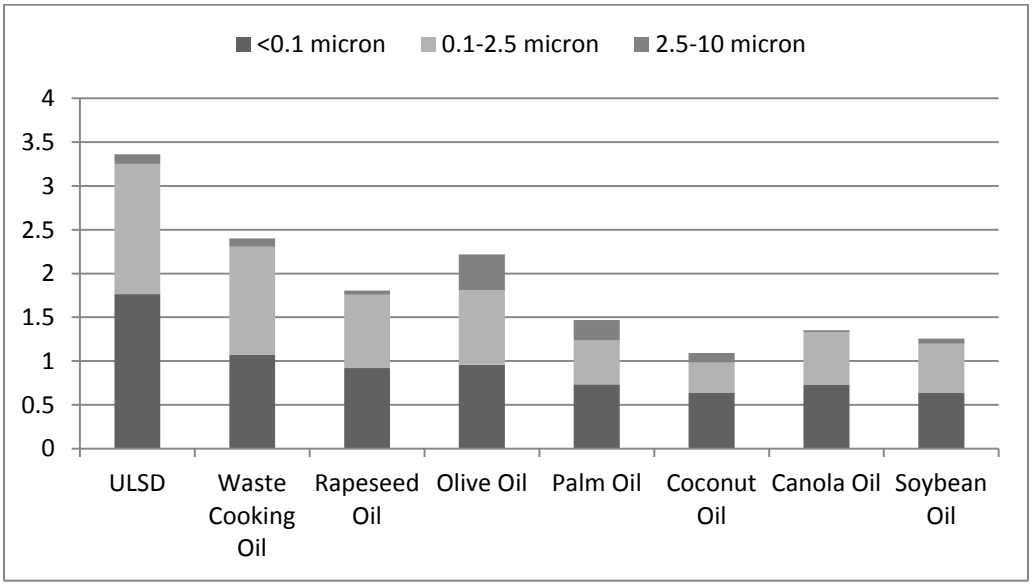


TABLE 9 PM reduction by using biodiesels compared with ULSD

	Waste Cooking Oil	Rapeseed Oil	Olive Oil	Palm Oil	Coconut Oil	Canola Oil	Soybean Oil
PM_{10} reduction(%)	28.6	46.3	34.0	56.3	67.5	59.8	62.6
$PM_{2.5}$ reduction(%)	29.1	46.0	47.7	62.0	69.7	59.1	63.2

High temperatures in the engine and high oxygen content in fuel resulted in less PM, which was good, but at the same time, produced more NOx. The understanding of the NOx/PM trade-off is important in figuring out the optimum emissions reduction conditions. In our study, coconut oil, soybean oil and canola oil produced relatively less PM than other biodiesels, but relatively high NOx emissions; while olive oil, rapeseed oil and palm oil produced relatively more PM than other biodiesels, but relatively low NOx emissions. Waste cooking oil is an exception, as it had poor performance in both PM and NOx production.

3.4 Statistic analysis of engine cell tests

The correlations between biodiesel chemical characteristics and fuel emissions were investigated to find factors important to reducing emissions. First, partial combustion emissions (PM, CO, and HC) are highly correlated to the amount of oxygen. Research has shown that fuel oxygen has more effect than oxygen-enriched air [65]: almost all the soot emissions can be removed when the fuel oxygen content reaches 25-30% [66]. Figures 11- 13 show the relationship between biodiesel oxygen content and

PM/CO/HC, and Table 10 summarizes p-values from analysis of variance (ANOVA) regression analysis of biodiesel oxygen content and emissions. PM data were only collected at 25% load, while the CO and HC emissions were monitored at every load. Both PM and HC had significant correlation with biodiesel oxygen content, but this was not true for CO emissions. However, with increased engine load, the correlation between CO and biodiesel oxygen content became stronger. As discussed in Section 3.3, the behavior of coconut oil CO and HC emissions was interesting. Here again, both on Figure 12 and 13 (only data for 25% and 75% tests were shown as representatives of low load and high load), we could see that coconut oil was a unique case. These results are consistent with a previous study also showing higher CO from coconut oil than from palm oil [67]. More CO and HC from coconut oil might be a result of smaller molecules in the fuel, with short chain fatty acids tending to form gaseous emissions rather than PM (coconut oil produced the least PM in all fuels).

The relationship between emissions and biodiesel H:C ratio, unsaturation degree, chain length, density, viscosity, and energy content were also analyzed. The unsaturation degree and chain length were calculated according to fatty acids ratio in every biodiesel based on the GC-MS data. Table 11 presents part of the results that show significant relations based on ANOVA analysis. In our study, HC was the component most affected by the fatty acids structure, both chain length and unsaturation degree. The relationships between fuel components and PM and CO were not that strong, despite some published researches supporting these connections [65, 68, 69]. However, in most of these studies, they only tested two or three biodiesel from different sources, while we have seven here with more complicated combinations of fatty acids.

Figure 11 Relation between PM and biodiesel oxygen content

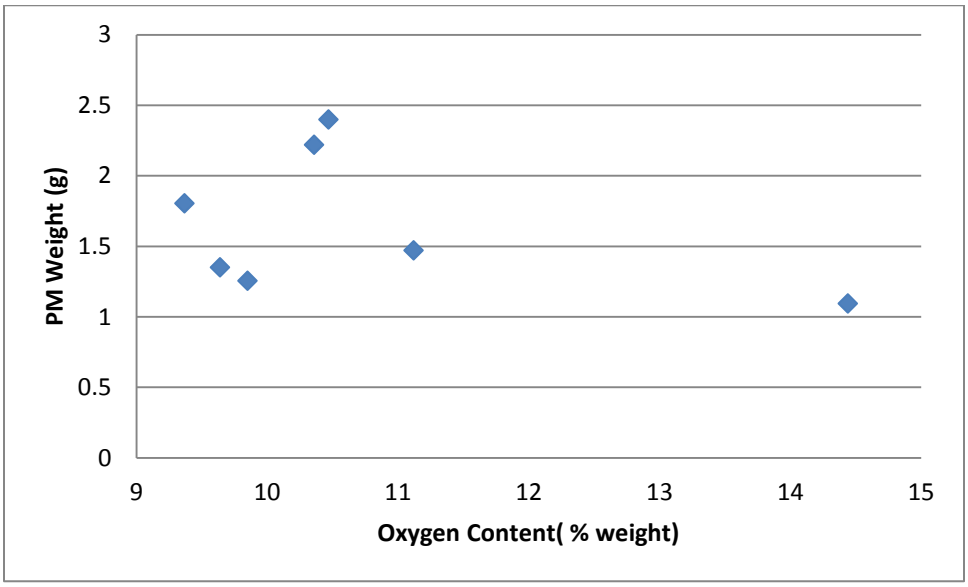


Figure 12 Relation between CO and biodiesel oxygen content

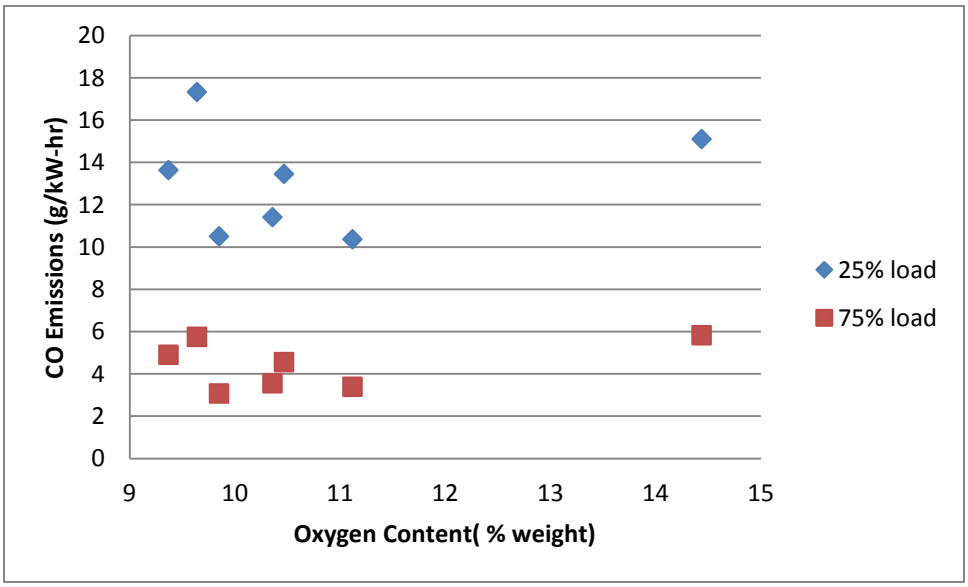


Figure 13 Relation between HC and biodiesel oxygen content

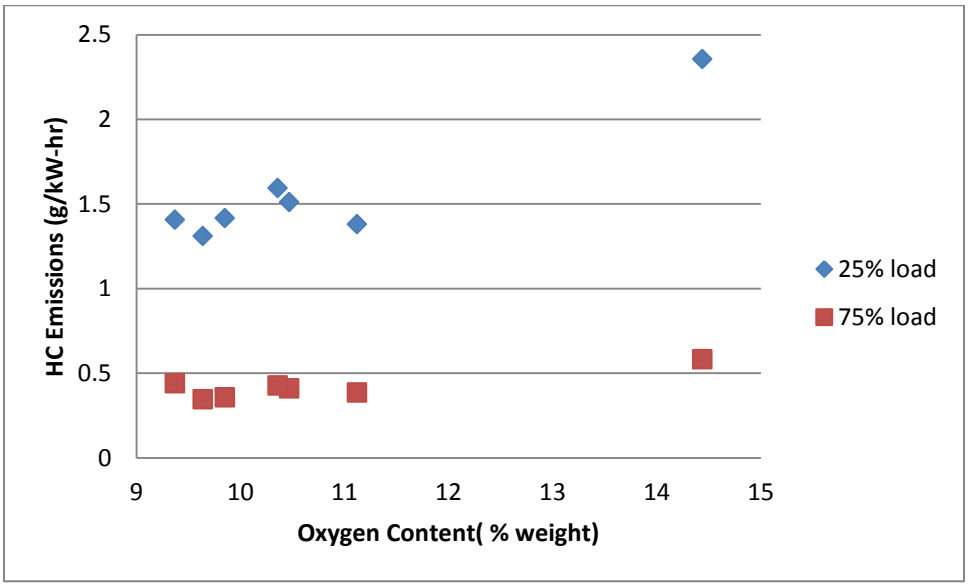


TABLE 10 Regression analysis of biofuel oxygen content and partial combustion emissions (p-value)

	0% load	25% load	50% load	75% load	100% load
PM	N/A	**0.0372**	N/A	N/A	N/A
CO	0.838	0.756	0.465	0.433	0.352
HC	**0.013**	**0.002**	**0.008**	**0.015**	**0.004**

TABLE 11 Regression analysis of biodiesel chemical characteristics and partial combustion product emissions (p-value)

	0% load	25% load	50% load	75% load	100% load
Energy content and HC	**0.005**	**0.001**	**0.004**	**0.029**	**0.001**
Energy content and CO_2	0.182	**0.004**	**0**	**0**	**0.001**
H:C and HC	0.177	0.067	0.137	0.069	0.105
unsaturation degree and HC	0.121	**0.032**	0.056	**0.037**	**0.029**
chain length and HC	**0.027**	**0.012**	**0.033**	0.09	**0.013**

Although not a regulated pollutant source, O_2 was monitored during each test the same as other emission gases, and from it we could have a general estimation of how much oxygen in air was used for the combustion. Oxygen in the exhaust was in proportion to biodiesel oxygen content, and was in inverse proportion to CO and HC emissions according to the regression analysis shown in Table 12. The relationship between gaseous oxygen and CO emissions was the most significant.

TABLE 12 Regression analysis of oxygen emissions (p-value)

	0% load	25% load	50% load	75% load	100% load
Oxygen content and O_2	0.208	0.232	0.127	0.123	**0.039**
O_2 and CO	**0.039**	0.087	0.052	**0.020**	**0.008**
O_2 and HC	0.177	0.067	0.137	0.069	0.105

The production of NOx depends on the temperature of the engine chamber and the oxygen concentration, so all factors which may affect these two points can affect NOx emissions. Examining the NOx emissions data (Figure 8-10) and the table of biodiesel components (Table 8), we can see that: (1) the more the biodiesels are saturated, the less NO were formed. Ex. palm oil and coconut oil, which had more saturated fatty acids produced less NO than other fuels; (2) the longer the fatty acid chains in biodiesel, the more NO were formed. Ex. rapeseed oil had more than 50% of C22 and the NO emissions from it were high, while coconut oil and palm oil which had more short chain fatty acids produced low NO emissions; (3) the degree of saturation of the biodiesel did not strongly affect NO_2 emissions; (4) biodiesels with long chain fatty acids (like rapeseed oil) produced less NO_2 than those with short chain fatty acids (like coconut oil). All biodiesel H:C ratio, the ratio of saturated fatty acids in biodiesel, and the biodiesel unsaturation degree could reflect the saturation degree of biodiesels. The Pearson Correlation between them and NO and NO_2 were calculated in Table 13. It showed that the biodiesel unsaturation show some indication of linear correlation with NO production. Figure 14 presented NO concentration vs. H:C ratio, and ULSD data was included, showing ULSD data didn't match the trends from the biodiesel fuels. Pearson Correlation of biodiesel chain length and NO and NO_2 were also calculated in Table 13.

Overall, the performance of coconut oil was substantially different from all of the other biodiesels. It had the highest oxygen content, and the most saturated fatty acids, however, the CO, HC and NO emissions from it were not as low as expected. This may be because of a plateau effect, or the composition of coconut oil was too different from other biodiesels, making it as a unique sample in our study.

TABLE 13 Pearson correlation of biodiesel characteristics with NO and NO_2

	NO					NO_2				
	0%	25%	50%	75%	100%	0%	25%	50%	75%	100%
H:C	-0.34	-0.85	-0.80	-0.82	-0.76	0.31	0.18	0.06	-0.01	-0.03
unsaturation degree	0.55	0.88	0.82	0.85	0.80	-0.37	-0.35	-0.28	-0.24	-0.23
saturation ratio	-0.30	-0.80	-0.72	-0.78	-0.76	0.57	0.46	0.35	0.26	0.21
chain length	0.24	0.74	0.67	0.74	0.77	-0.81	-0.74	-0.64	-0.50	-0.39

Figure 14 Relation between H:C ration and NO emissions

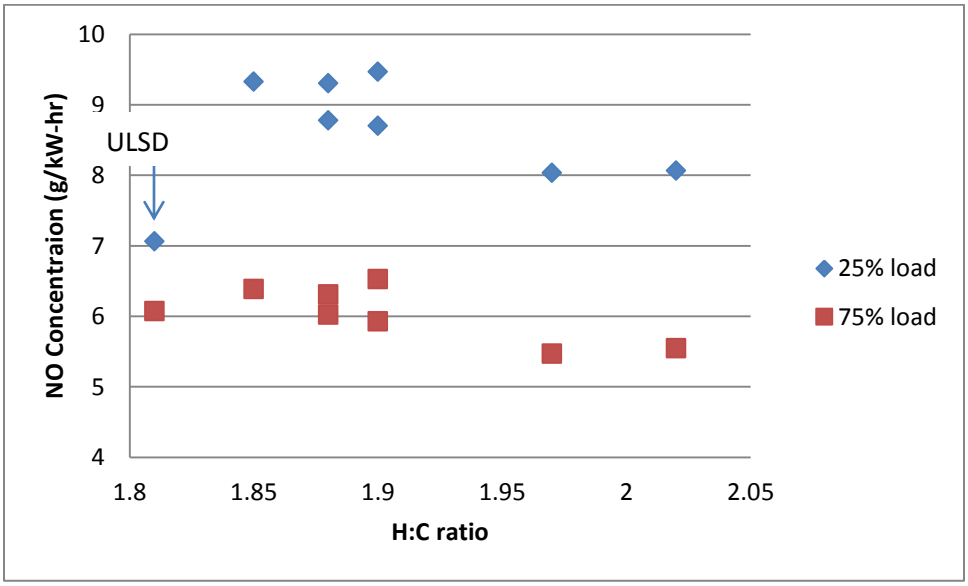


Table 14 lists factors that were strongly correlated with NOx based on ANOVA regression, and shows the p-value of each regression analysis. The degree of saturation of the biodiesel affected NO production, and biodiesel oxygen content and fatty acids chain length also were correlated with NO production. Biodiesel oxygen content, fatty acids chain length and biodiesel energy content had strong correlations with NO_2 production at low loads, but the correlations were not that significant at high loads. Biodiesel density had strong relationship with NO and total NOx concentrations, as experiments showed

that the density of fatty acids decrease with increasing chain length and the level of unsaturation [70]. In this way, density measurement is a convenient way to estimate NO and total NOx production.

TABLE 14 Significant results from ANOVA regression on NOx emissions (p-value of regression analysis).

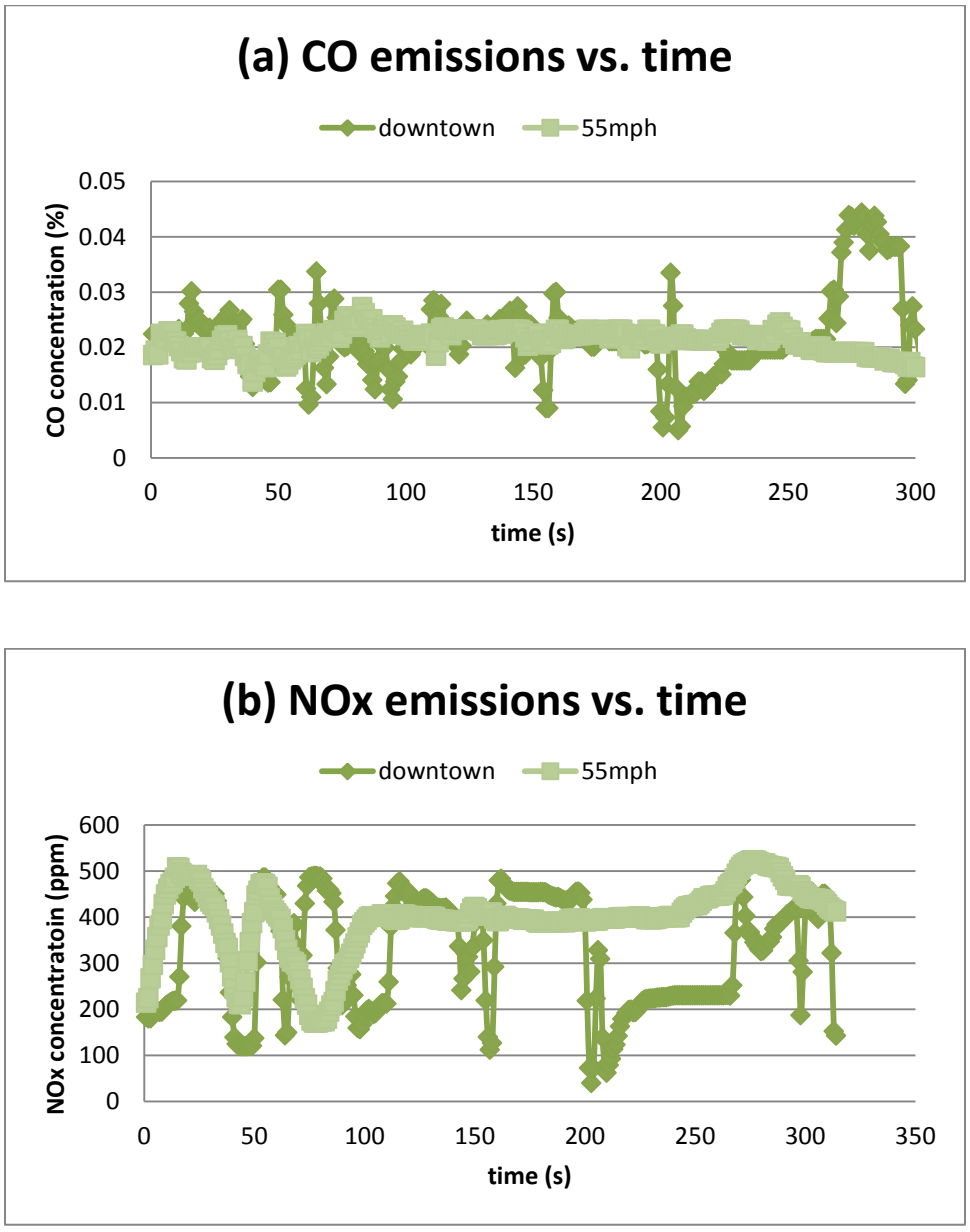
Factors correlated to NO emission					
	0% load	25% load	50% load	75% load	100% load
H:C ratio	0.461	**0.016**	**0.032**	**0.023**	**0.046**
Ratio of saturated fatty acids	0.513	**0.03**	0.066	**0.037**	**0.047**
Unsaturation degree	0.199	**0.01**	**0.023**	**0.017**	**0.032**
Biodiesel oxygen content	0.387	0.066	0.118	0.08	0.08
Average chain length of fatty acids	0.599	0.057	0.098	0.06	**0.042**
Biodiesel density	0.746	**0.009**	**0.008**	**0.007**	**0.009**
Biodiesel viscosity	0.682	0.114	0.116	0.09	**0.044**
Biodiesel energy content	0.453	0.124	0.176	0.137	0.109
Factors correlated to NO_2 emission					
	0% load	25% load	50% load	75% load	100% load
Biodiesel oxygen content	0.089	0.118	0.183	0.266	0.334
Average chain length of fatty acids	**0.027**	0.055	0.123	0.257	0.393
Biodiesel energy content	**0.024**	**0.025**	0.06	0.128	0.22
Factors correlated to NOx emission					
	0% load	25% load	50% load	75% load	100% load
Biodiesel density	0.92	0.088	**0.035**	**0.008**	**0.004**

The effect of fatty acids structures to NOx formation may be because of the prompt NOx formation, which relies on high concentrations of intermediate CH species. High levels of unsaturated compounds may result in more hydrocarbon radicals during combustion, thus producing higher NOx emissions [71]. At the same time, unsaturated molecules correlate to higher adiabatic flame temperature than saturated ones [71], therefore an increase of thermal NOx can also be expected.

3.5 Preliminary results from biotruck on-road tests

Data from on-road biodiesel truck tests are more complicated than from engine tests, and are difficult to analyze because emissions levels are influenced by road conditions that are hard to control. During the downtown test, we observed high levels of emissions when the truck is speeding up or climbing up hills because of the increased engine load. Even in highway tests (speed set as 55mph and 65mph), there are still significant changes in engine load and emission levels. Figures 15(a-c) showed emission concentrations along time of downtown and 65mph tests. The highway test was much more steady than the downtown test due to more consistent engine load conditions. Table 15 states the average values and standard deviations of engine information and emissions concentrations, which show that emissions levels from highway tests are more consistent than those from the downtown test.

Figure 15 Emissions (CO, NOx and HC) vs. time of downtown & 65mph tests



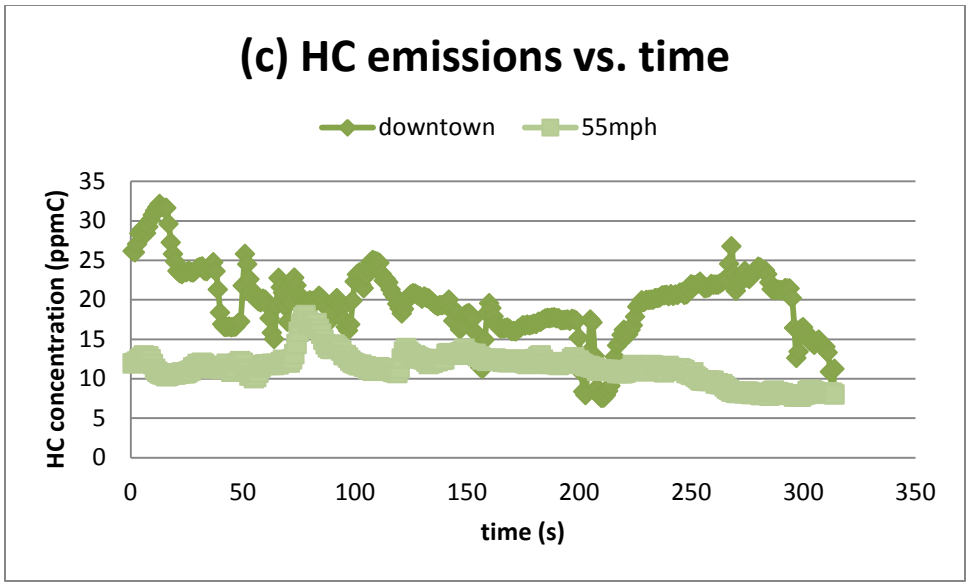


TABLE 15 Summary of three on-road tests

Scenario		Engine Speed rpm	Vehicle Speed mph	Engine Load %	CO_2 g/mile	CO g/mile	NO g/mile	NO_2 g/mile	NOx g/mile	HC g/mile
Downtown	Average	1258	27.6	18.1	896.4	3.34	8.00	0.0103	8.01	0.155
	Standard Deviation	393.2	15.4	9.84	49.3	1.28	3.12	0.0126	3.13	0.080
55mph	Average	1551	54.4	20.8	667.4	2.09	6.19	0.0160	6.21	0.0546
	Standard Deviation	5.848	0.429	6.44	0.7199	0.713	0.386	0.00860	0.390	0.0271
65mph	Average	1835	64.8	20.9	666.5	3.00	5.67	0.0520	5.72	0.0542
	Standard Deviation	7.365	0.381	6.23	2.510	0.409	0.844	0.0240	0.846	0.0109

From Table 15, we can see that the standard deviations of engine load for all three tests were high, which indicates a large variation in engine load during the tests; the engine speed changed a lot in downtown test, however, with the constant vehicle speed in the highway tests, the engine speed varied only slightly. These data told us that the vehicle speed is mainly related to the engine speed, rather than the engine load. Raw

emissions data (g/kg fuel) are translted here into emissions on a g/mile basis, a more common unit for on-road tests (g/mile = (g/kg fuel)*(kg fuel/gal)/(mile/gal)) . Because of the higher fuel consume in downtown (according to information provided by Dr. Williams group, averagely, the biotruck drove 12 mile per gallon in downtown, and 16 mile per gallon on highways), the emissions from downtown test were higher than them from highways tests, except NO_2. Comparing the two highway tests, higher engine speed resulted in higher CO and lower NOx emissions. In order to investigate trends of tailpipe emissions better across tests, we would like to figure out a new parameter that combines all effects on emission levels.

The first is torque, which is related to engine speed and engine load. In our engine tests, engine speed was constant, and once engine load was controlled, the torque was determined. So we could use engine load to discover emissions trends instead of torque. Unfortunately, the protocol we used for our Semtech vehicle interface didn't support getting torque data directly. In order to get torque according to engine speed and engine load, an engine torque map is need. However, so far we don't have one for this particular engine.

The other parameter that can be used is vehicle specific power (VSP). VSP is an on-road power output variable that is based on road, driving, and vehicle physical variables. It is used by EPA for current emissions modeling work. Figure 16 provides the concept of how VSP is defined and derived (VSP is the sum of aerodynamic drag, acceleration, rolling resistance, and hill climbing divided by the mass of vehicle). With assumptions of mass factor, coefficients, vehicle physics, and air density, a simplified

equation for typical U.S. light-duty trucks is shown below[72]. According to this equation, when the vehicle is decelerating or driving downhill, the VSP can be very small or even negative. This negative VSP was common in the downtown test.

$$VSP = Power/Mass \approx 1.1 \cdot v \cdot a + 9.81 \cdot grade \cdot v + 0.213 \cdot v + 0.000305 \cdot (v + v_w)^2 \cdot v$$

In which

VSP = vehicle specific power, kW/Metric Ton

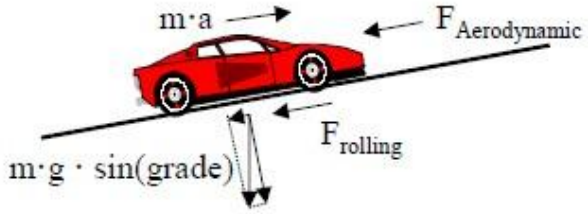
v = vehicle speed, m/s

v_w = headwind into the vehicle, m/s. In our study, wind data are not recorded, therefore v_w is set as zero.

a = acceleration, m/s^2

grade = vertical rise/horizontal distance

Figure 16 Vehicle specific power



$$VSP = \frac{Power}{Mass} = \frac{\frac{d}{dt}(E_{Kinetic} + E_{Potential}) + F_{Rolling} \cdot v + F_{Aerodynamic} \cdot v + F_{internal\ friction} \cdot v}{m} =$$

$$\approx v \cdot a \cdot (1 + \varepsilon_i) + g \cdot grade \cdot v + g \cdot C_R \cdot v + \frac{1}{2} \rho_a C_D \frac{A}{m} (v + v_w)^2 \cdot v + C_{if} \cdot v$$

in which,

ε_i = mass factor, the equivalent translational mass of rotating powertrain components, (dimensionless)

g = gravity acceleration (9.81 m/s^2)

C_R = coefficient of rolling resistance (dimensionless)

C_D = drag coefficient (dimensionless)

A = cross-sectional area of the front of the vehicle

m = vehicle mass

ρ_a = density of ambient air (kg/m^3)

In highway tests, once the vehicle speed is set, engine speed keeps at a mostly steady value during the test time, and engine load becomes the only variable. Figure 16(a-b) present the relationship between the calculated VSP and recorded Engine load. The amount of work needed to keep the vehicle moving (VSP) determines how hard the engine is needed to work (engine load). The trends in Figure 17(a) and (b) were similar in that VSP positive related to engine load with around 5 kW/Metric Ton varied range, and the 65mph test had a bigger slope, which was predictable according to the VSP equation we used (every term in the equation has velocity in it).

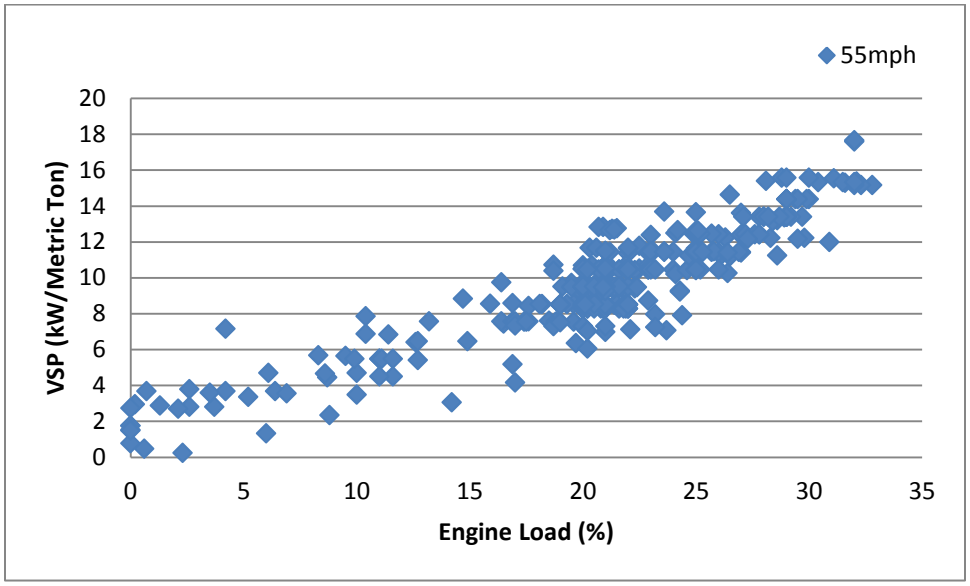
Figure 18-20(a-d) show the emissions versus VSP for three on-road tests separately. VSP was the power required to keep vehicle moving, and it was calculated based on the change of vehicle kinetic energy and potential energy, which means it can be either positive or negative. For the downtown test, most of the negative VSP measurements happened when the truck was slowing down, or driving down on the hill; while in highway tests, because that the speeds were controlled well (less than 1mph error) and there was no evident deceleration or downhill , the calculated VSP were almost all positive. From the results of highway tests (both 55mph and 65mph), we found out that partial combustion emissions (CO and HC) had lower levels at high VSP. The reduction was more obvious when VSP is lower than 5 kW/Metric Ton, and then the decreasing rate slowed down, and finally reached zero. At high VSP area, CO and HC concentrations were affected more by random uncertainty. Furthermore, the 55mph test produced less CO than 65mph at high VSP area, and had bigger slope of decreasing of HC than 65mph test. However, unfortunately, we didn't see obvious trends of NOx according to the change of VSP, except NO emissions from both tests mainly

concentrated between 24-32 g/kg fuel, and 65mph test had significant higher level NO_2 emissions. Also, no trends were found for the downtown test which had too many affecting factors.

With the trends of CO and HC from highway tests, VSP is proven to be one parameter affecting partial combustion emission concentrations, also, we see that the formation of NOx is much more complicated than CO and HC, and there is no way to analyze it better according to our data in hand.

Figure 17(a-b) Relationships between VSP and Engine Load of highway tests

(a)



(b)

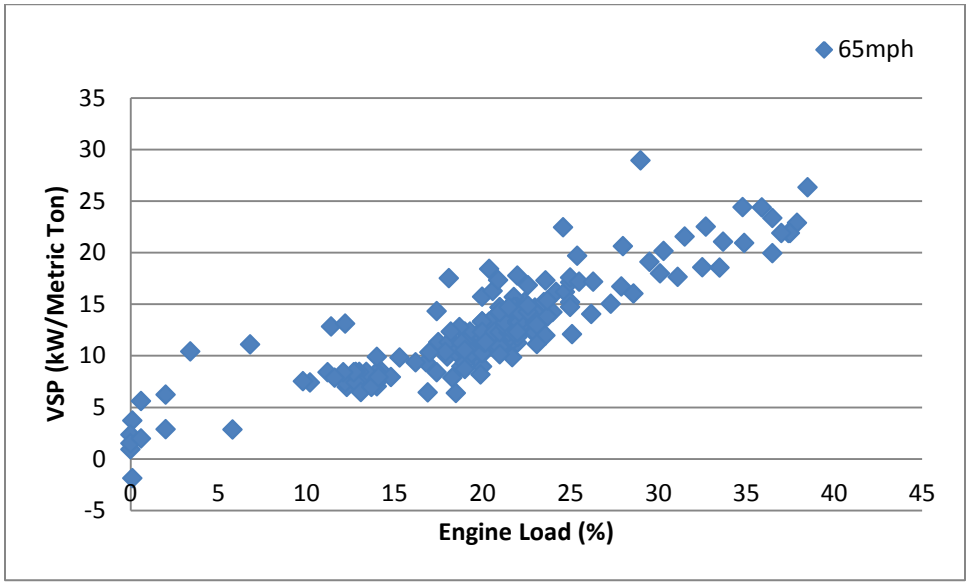
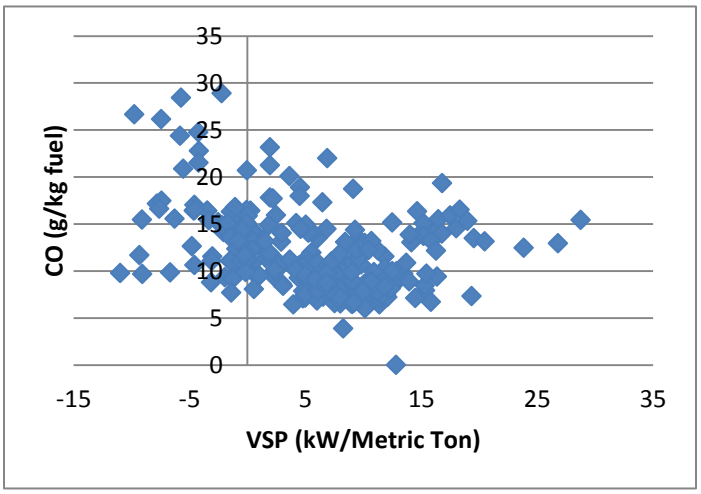
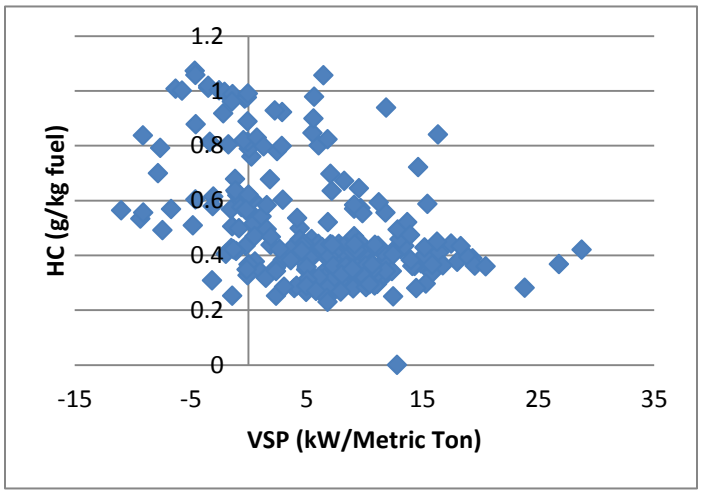
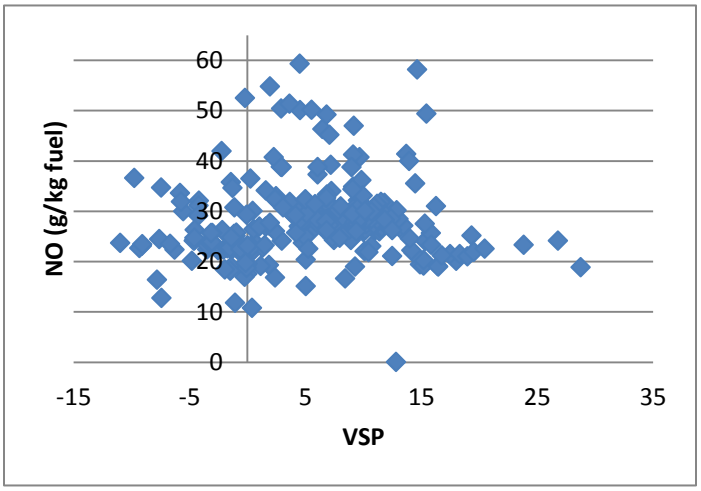


Figure 18(a-d) Emissions vs. VSP for downtown test







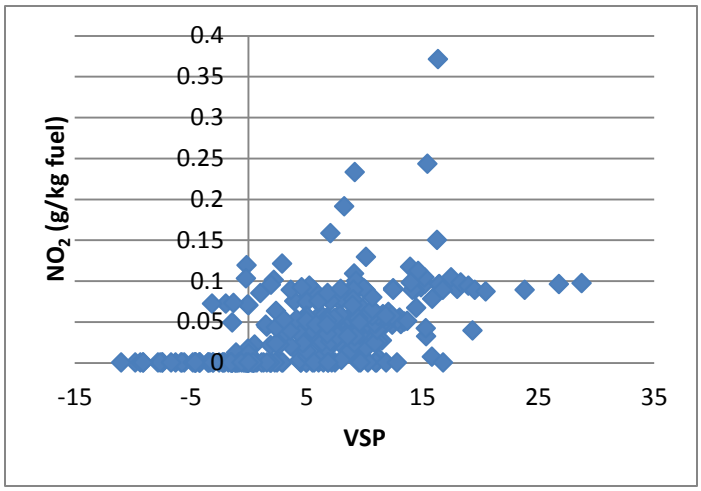
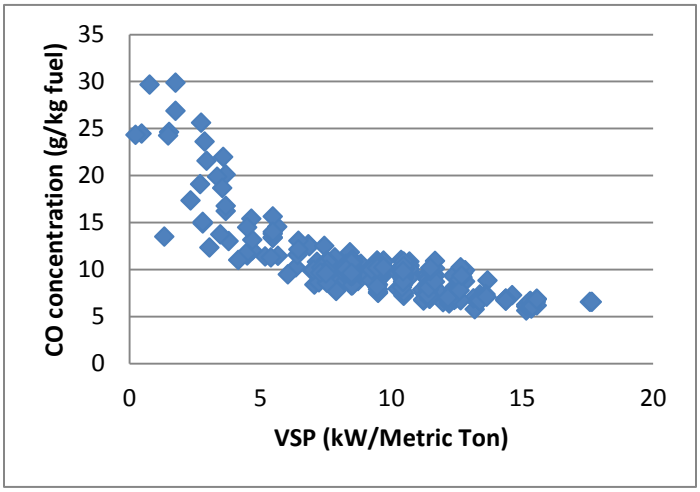
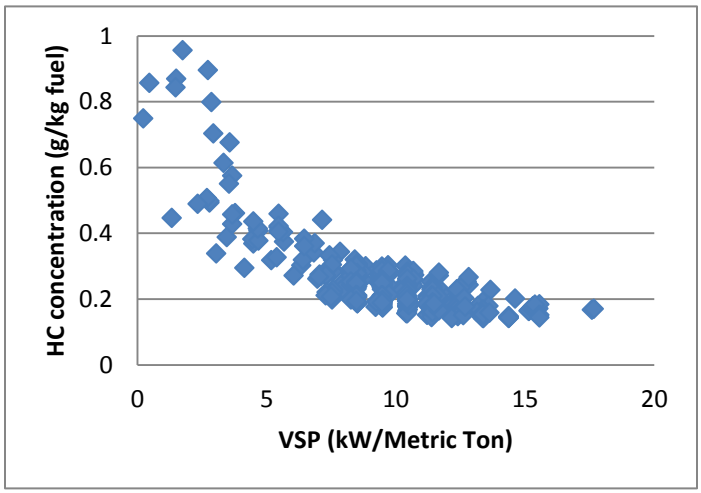
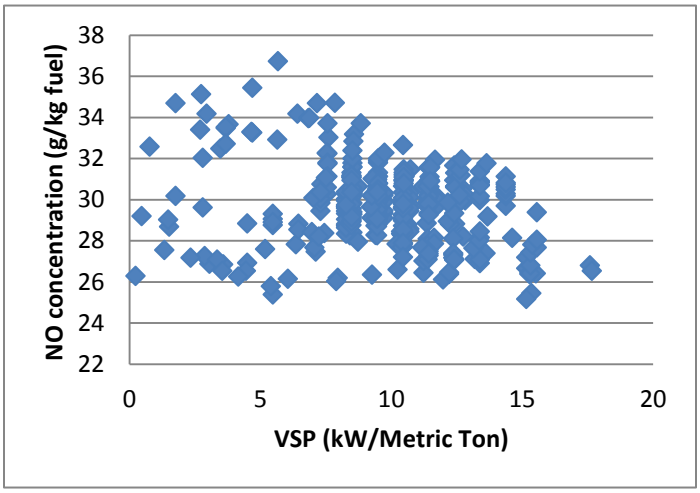


Figure 19(a-d) Emissions vs. VSP for highway test (55mph)







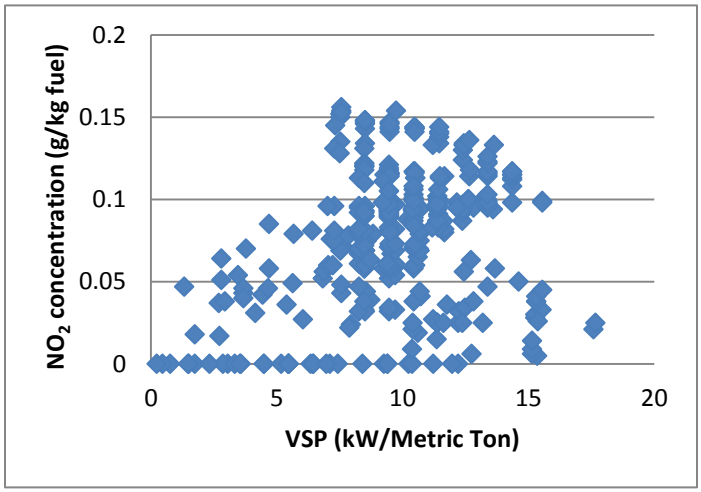
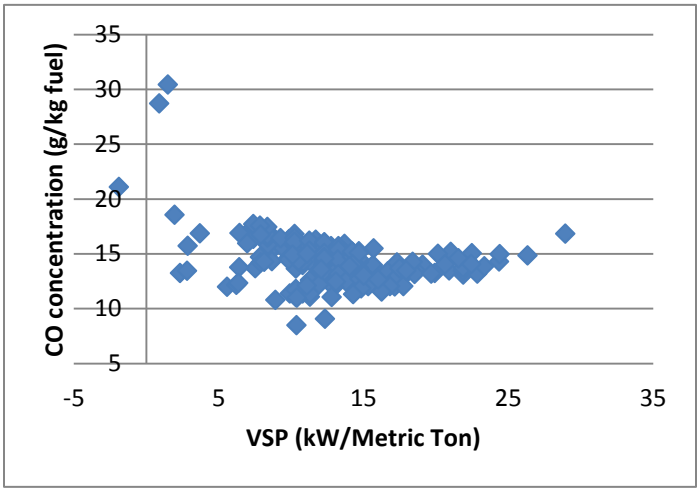
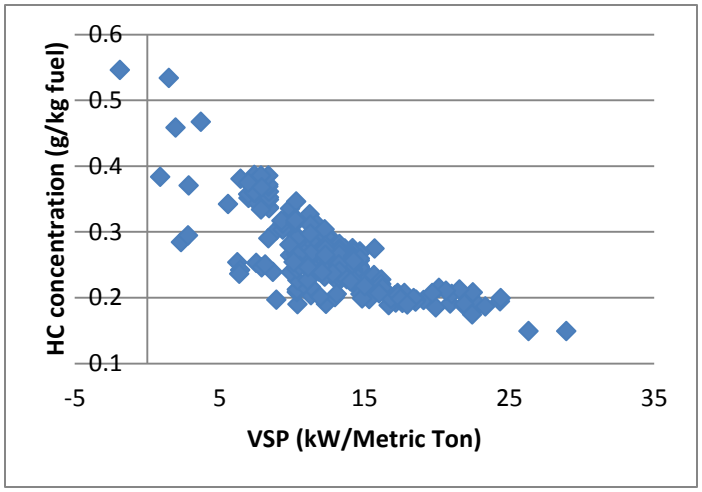
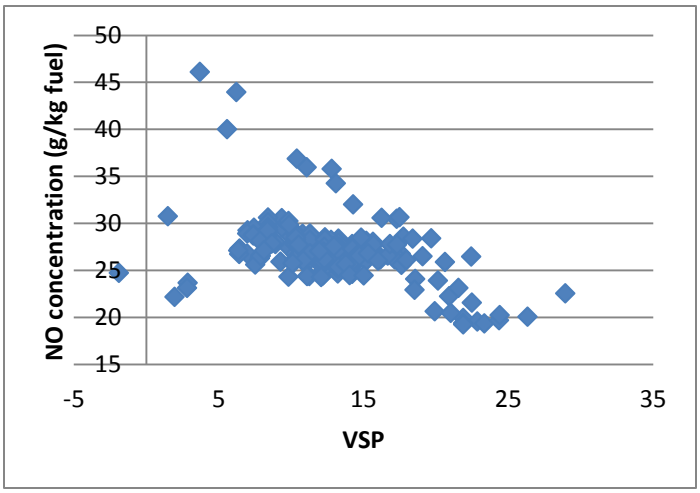
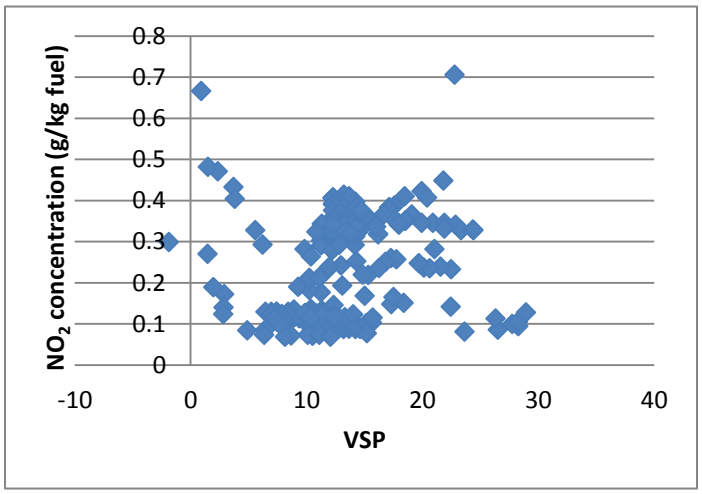


Figure 20(a-d) Emissions vs. VSP for highway test (65mph)









Chapter 4

Conclusions and Future Work

This study tested and analyzed ULSD and seven biodiesels (waste cooking oil, rapeseed oil, palm oil, olive oil, coconut oil, canola oil, and soybean oil), for their chemical properties, components structures, and emissions while run on a single cylinder diesel engine. The advantage of low emission levels when using biodiesels compared with using ULSD was discovered, and how the biodiesel components affecting emissions were found out. After the engine tests, we also did several on-road test with waste cooking oil biodiesel to figure out a way of better collecting and understanding on-road data.

4.1 Fuel chemical characteristics

Our chemical analysis of biodiesels showed that biodiesels had higher H:C molar ratio, higher oxygen content, slightly higher density, greater viscosity, and lower energy content compared to ULSD. The average oxygen content in biodiesels was above 10%, which was very important to emissions formation, not only to partial combustion emissions as PM, CO and HC, but also to NOx. Energy content was very important because it determined brake specific fuel consumption and therefore affected emission concentrations according to our calculation. Among all of the biodiesels, rapeseed oil had highest energy content while coconut oil had smallest energy content, and the average

energy content of biodiesels was about 87% of ULSD. Meanwhile, the composition of the biodiesels was analyzed. Results showed that biodiesels from different sources had very different compounds of fatty acids, including the number of double bonds and fatty acids chain length. Coconut oil was the most saturated of all the biodiesels, with more than 90% saturated fatty acids. At the same time, it was the one with more short chains than other fuels, with more than 70% of C12 and C14. Soybean oil was the one least saturated, and rapeseed oil had longer chains than others with 56% of C22 and 40% of C18. Both the double bonds (unsaturation degree) and chain length affected NOx formation significantly, as discussed later.

4.2 Engine tests

Seven biodiesels and ULSD were run on a single cylinder engine, with constant engine speed of 3600rpm. For each fuel, we ran five tests at different loads (0%, 25%, 50%, 75% and 100%), and collected engine performance data and emissions data for each test. Because of the low energy content in biodiesels compared with ULSD, all biodiesels had higher BSFC than ULSD. BSFC decreased with the increase of engine load. Rapeseed oil had the lowest BSFC among all biodiesels (12% higher than ULSD), and coconut oil had the highest BSFC.

PM reduction from biodiesels compared with ULSD was obvious. Coconut oil produced the least PM in all fuels, which was only about 30% of ULSD; waste cooking oil produced the most PM among biodiesels, but still was only 70% of ULSD. According

to the statistical analysis, PM was highly correlated to biodiesel oxygen content: the higher fuel oxygen content, the less PM was produced. Biodiesels also produced less partial combustion gases, both in CO and HC. All biodiesels had less CO than ULSD at low engine load, but some produced higher CO than ULSD at high engine load. Biodiesels had better performance for HC formation than ULSD except coconut oil. HC concentrations from biodiesels had strong relationship with fuel oxygen content, H:C molar ratio, unsaturation degree, and fatty acids chain length, however, no significant effect of fuel characteristics to CO production was discovered.

In our study, it is not always true that biodiesel produced more NOx than ULSD. ULSD produced less NO at 25% load, but some biodiesels started to show advantage with increased engine load. All biodiesels produced less NO_2 than ULSD at all loads. For total NOx, NO was the main part of NOx; palm oil produced the least NOx in all fuels and waste cooking oil produced the most. Our result showed that NO was strongly related to the biodiesel components. All parameters reflecting double bonds in fuels could be used to estimate NO production, including H:C ratio, ratio of saturated fatty acids and unsaturation degree. Biodiesel oxygen content and fatty acids chain length also affected NO. Density was also an easy way to forecast NO formation.

4.3 On-road tests

Our on-road tests of using biodiesels are still on a very beginning stage. We found that speed was not the major factor influencing emission levels, especially when fuel

consumption rate was considered. The downtown test produced more emissions per mile than highway tests. In order to take both engine load and engine speed into account, we tried to use VSP to investigate emissions trends, and found out that the production of CO and HC decreased when VSP was increasing, but this trend disappeared when VSP was high at a certain level. No significant relationship between VSP and NOx was discovered.

4.4 Future work

So far, our study results meet our expectations well. Biodiesel composition did affect emissions, and palm did have reduced NOx. Also, we successfully made several on-road tests, helping develop a method for future emissions testing. In the future, we would like do further testing to get better understanding of emission reductions from biodiesels, with the use of palm oil (it has the best performance on reducing emissions), soybean oil and rapeseed oil (they are commonly used in U.S. and Europe currently due to availability and economic concerning). The following are some suggested avenues for future work:

In the engine cell:

(1) We are planning to run more tests using biodiesel blends, especially the blends of palm oil and ULSD, palm oil and other biodiesels, to investigate the relationship between blend ratio and emission levels: is it linear or nonlinear; is it exponential or logarithmic, etc, in order to make economic blends producing low emissions on a large scale.

(2) We would like to collect more engine data in engine tests, including in-cylinder temperature and pressure, to help further understand emissions formation, particularly to figure out the relationship between different emissions, for example, the trade-off between NOx and PM. This will help determine the best operation situations for maximizing emissions reductions.

(3) It will be interesting to explore further the effect of fuel oxygen content with the adding of oxygenates, both on PM and NOx formation.

For on-roads tests:

(1) Considering so far we haven't found a relationship between VSP and NOx by using the current data, we'll try to get the engine torque map of our truck to see the relationship between torque and VSP. This will allow for better correlation of emission with engine performance.

(2) If we stick with using VSP, we would like to improve our calculation of it. For example, adding wind data or using more detailed equation with the physical parameters of our biotruck. Also, it might be a good approach to try averaging emission concentration in a small range of VSP, see if we can get some trends.

(3) In order to compare data sets better, tests with different fuels and speed should be arranged well on the same route to minimize variable factors (traffic, driver activity, etc.), and therefore help us to find out the effect of different fuels, as well as the effect of vehicle speed. After that, several routes can be developed to see whether topography will affect emissions.

(4) Emission concentrations may vary with ambient temperature, pressure, and humidity, therefore, more tests would be run different time in a year, or under different weather.

(5) It is possible to modify the truck tailpipe, making it compatible with our flowmeter, to get the total mass of emissions, which can help us to calculate total tailpipe emissions with different fuels and fuel blends.

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